



**Yazawa International Symposium  
METALLURGICAL AND MATERIALS PROCESSING:  
PRINCIPLES AND TECHNOLOGIES**

**Convention Center/Marriott Hotel  
San Diego, California, USA  
2-6 March 2003**

**FINAL PROGRAM**



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of Utah



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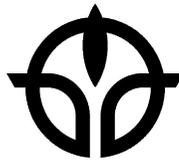


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## YAZAWA INTERNATIONAL SYMPOSIUM PROGRAM GRID

Monday March 3		Tuesday March 4		Wednesday March 5		Thursday March 6	Room
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	Recycling, Waste Treatment and Environmental Issues I	Recycling, Waste Treatment and Environmental Issues II	Recycling, Waste Treatment and Environmental Issues III	Iron and Steel Making Fundamentals I	Iron and Steel Making Fundamentals II	Iron and Steel Making Fundamentals III and Applications	Leucadia Marriott Hotel
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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Plenary

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee, Co-Sponsors: ASM International; Asociación Argentina de Materiales/Materials Research Society of Argentina; Associação Brasileira de Metalurgia e Materiais; Associazione Italiana di Metallurgia; Australasian Institute of Mining and Metallurgy; Chinese Metals Society; Czech Society for New Materials and Technologies; Dansk Metallurgisk Selskab/Danish Metallurgical Society; Deutsche Gesellschaft fuer Materialkunde; Dowa Mining Co., Ltd.; European Journal of Mineral Processing and Environmental Protection; Federation of European Materials Societies; Finnish Association of Mining and Metallurgical Engineers; FLOGEN Technologies, Inc.; Furukawa Co., Ltd.; Institute of Materials (UK); Institution of Mining and Metallurgy; Instituto Argentino de Siderurgia; Instituto de Ingenieros de Minas de Chile; Iron & Steel Institute of Japan; Iron & Steel Society; Japan Institute of Metals; Korea Zinc Co. Ltd., Korean Institute of Metals & Materials; Metallurgical Society of the Canadian Institute of Mining, Metallurgy and Petroleum; Mining and Materials Processing Institute of Japan; Mitsubishi Materials Corporation; Mitsui Mining and Smelting Co., Ltd.; Nippon Mining & Metals Co., Ltd.; Non-ferrous Metals Society of China; Outokumpu Oyj, Finland; Slovak Metallurgical Society; Slovensko drustvo za materiale/Slovenian Society of Materials; Société Française de Métallurgie et de Matériaux; Society for Mining, Metallurgy, and Exploration; South African Institute of Mining & Metallurgy; Sumitomo Metal Mining Co., Ltd.; Toho Zinc Co., Ltd.  
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Monday AM Room: 6D  
March 3, 2003 Location: San Diego Convention Center

*Session Chairs:* Hong Yong Sohn, University of Utah, Dept. of Metallurg. Eng., Salt Lake City, UT 84112-0114 USA; Florian Kongoli, FLOGEN Technologies Inc., Montreal, Quebec H3S 2C3 Canada

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### 8:30 AM Hong Yong Sohn: Opening Remarks

### 8:45 AM Plenary

**Lifetime Achievements of Prof. Akira Yazawa:** *Kimio Itagaki*<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

The lifetime achievements of Prof. Yazawa, one of the most quoted authors in pyrometallurgical reference books worldwide, are respectfully highlighted and summarized with a bird's-eye view. His research works, published in more than 300 technical papers in the last 50 years, started with the mutual dissolution of copper matte and iron silicate slag, continued with a variety of subjects related to slags, alloys, matte, speiss, aqueous solutions, alcohols and alga and are still continuing in several fields including the thermodynamic calculation of the dioxine formation. This colorful activity, recognized worldwide with many awards, prizes and honors, is categorized according to various disciplines such as thermochemistry, chemical metallurgy, process metallurgy and extractive metallurgy of numerous nonferrous metals. His close collaboration and cooperation, in research and education, with many domestic and international fellows, research associates, students and metallurgical engineers is also highlighted as a great achievement of Prof. Yazawa especially when it is noted how wide and deep this relationship and friendship developed and continuously grew over the years.

### 9:20 AM Plenary

**Contribution of Copper Smelting Technology to Preserving Global Environment:** *Akira Nishikawa*<sup>1</sup>; <sup>1</sup>Mitsubishi Materials Corporation, Tokyo 100-8117 Japan

During the twentieth century, the copper smelting industry achieved dramatic expansion corresponding to the vast growth of global economy. This was largely due to innovations in pyro-metallurgical processes, such as autogenous smelting and continuous smelting and converting technologies. However, as copper production capacity increased, its impact on the environment also could not be ignored, and thus with increasing global environmental awareness, many smelting operations either had to renew or rebuild their facilities. In addition to these changes, in places like Japan and Europe, with scarce primary resources, the treatment and recovery of metals from items such as car shredder dust, used electrical appliances and electronic devices, on top of scraps traditionally treated, is having a profound effect on the reduction and neutralization of waste. Thus compared to the days when copper smelting focused on the environmental control in order to break with "Smoke Stack Industry", copper smelting today is making an important contribution to preserving the global environment.

### 9:55 AM Plenary

**Impurity Capacity of Non-Ferrous Metals Production Slags:** *Ramana G. Reddy*<sup>1</sup>; <sup>1</sup>The University of Alabama, Ctr. for Green Mfg., Dept. of Metallurgl. & Matls. Eng., Tuscaloosa, AL 35487 USA

A Modeling and Experimental study on impurity capacity and distribution between mattes and slags in sulfide smelting of non-ferrous metals was discussed. A Thermodynamic model for prediction of impurities capacities in slags and their distribution in mattes and slags was developed. The impurities capacities (i.e. sulfur and arsenic) of slags were calculated a priori using modified Reddy-Blander model. The capacities predictions were made in a wide range of matte and slag compositions,  $PSO_2$  and temperatures in copper, nickel and lead smelting conditions. The calculated results for sulfur and arsenic capacities are in good agreement with the available experimental data. Application of this model for the prediction of Sb, Bi and other impurities capacities and distribution ratios in mattes and slags, and removal of impurities in several industrial smelter processes is discussed.

### 10:30 AM Break

### 10:40 AM Florian Kongoli: Plenary Remarks

### 10:55 AM Plenary

**Application of Sodium Carbonate Slag to Copper Refining:** *Chikabumi Yamauchi*<sup>1</sup>; <sup>1</sup>Chubu University, Grad. Sch. of Eng. & Sch. of Eng., 1200 Matsumoto-cho Kasugai-shi, Aichi-ken 487-8501 Japan

An outline of the following will be given. (1)Prof. Akira Yazawa as our pride. (2)Predominance of the application of sodium carbonate slag to copper refining in comparison with that to pig iron refining. (3)Not experimentally direct measurement of the distribution ratios of impurity elements such as As, Sb, etc. between sodium carbonate slag and molten copper, but indirect calculation of them by using thermodynamic data which were measured by our own experiments. (4)Reasons why such an approach was accepted. (5)Principle of the calculation. (6)Examples of results and discussion. (7)Approach for reducing the contents of impurity elements to their desired levels(Comparison of the calculated values with those obtained by experiments). (8)Kinetic aspects.(9)Application of the slag to a practical operation. (10)future view.

### 11:30 AM Plenary

**Non Ferrous Metals—The Challenges in Production and Technology Transfer:** *Juho Mäkinen*<sup>1</sup>; <sup>1</sup>Outokumpu Oyj, Riihitontuntie 7B, PO Box 140, Espoo 02200 Finland

Non-ferrous metals and metals in general are considered as being non-renewable natural resources. This is naturally true, but the predictions that the world would within a short period of time run out of metals have proven to be highly exaggerated. Metals are needed because of their excellent and irreplaceable properties. The consumption of metals, with the exception of carbon steel, is steadily growing by 1-3% annually, and that of stainless steel as much as 3-6%. This is a general trend, which it is periodically disturbed by cyclical variations. In recent years so-called "NEW ECONOMY" has become prominent in the public media and the market value of the traditional industry has been well below its real value and importance. Nevertheless, the modern society requires metals today and also in the future, and the companies using the most modern technology in a responsible way and innovative solutions not only in technology, but in everything they do will survive. Outokumpu Oyj is one of the leading metals and technology companies in the world in stainless steel, copper, zinc, and sales of technology in metals and minerals businesses. Outokumpu applies its knowledge of metals and metals processing to generate value for its customers and shareholders. Everything we do, we do in an economically, environmentally and socially responsible way.

## 12:05 PM Plenary

### The Role of Lead Smelting at Korea Zinc: *Chang-Young Choi*<sup>1</sup>;

<sup>1</sup>Korea Zinc Company, Ltd., Young-Poong Bldg., 142 Nonhyon-dong Gangnam-ku, Seoul 135-749 S. Korea

Korea Zinc Company commenced zinc production in 1978 with a capacity of 50,000 tpa. Since then, continuous investments have been made and resulted in Korea Zinc now being the biggest zinc and lead producer in the world. In the course of increasing zinc production capacity, the company management realized that the company needed a lead smelter to prevent the solid waste disposal problems by treating the lead containing solid waste. This paper begins by briefly stating the objectives and the roles of the lead smelter at Onsan. It describes the QSL process and the TSL process, and further extends the description of the TSL process, through which harmless inert solid waste could be produced for secure final disposal. It is also mentioned that the TSL process plays an important role in the integration of zinc and lead production. Throughout the paper, a positive attitude in handling the environmental issues in the non-ferrous smelting industry is emphasized. Finally, a solution for the solid waste disposal problem in the zinc and lead industry is proposed, with which the environmental issues can be an opportunity rather than a crisis. The current operation at Onsan suggests the future direction of the non-ferrous smelting technology that all of the zinc and lead producers should pursue.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Kinetics & Thermodynamics

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Monday PM  
March 3, 2003

Room: Solana  
Location: San Diego Marriott Hotel

*Session Chairs:* Derek J. Fray, University of Cambridge, Matls. Sci. & Metall., Cambridge CB2 3QZ UK; Hong Yong Sohn, University of Utah, Metallurgl. Eng., Salt Lake City, UT 84112-0114 USA

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## 2:00 PM Keynote

**Thermodynamics and Fluid-Solid Reaction Kinetics: Effects on the Rate and Activation Energy:** *Hong Yong Sohn*<sup>1</sup>; <sup>1</sup>University of Utah, Metallurgl. Eng., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA

The purpose of this article is to critically and quantitatively analyze the effect of chemical equilibrium on the overall rates of fluid-solid reactions. It is shown through a mathematical analysis that a reaction with a small equilibrium constant (a positive standard free energy of reaction) is more likely to be rate-controlled by pore diffusion or mass transfer than a reaction with a large equilibrium constant. The overall reaction rate of the former also tends to be slow. Furthermore, the apparent activation energy of such a reaction approaches the standard enthalpy of reaction, rather than the true activation energy of the chemical reaction. The Law of Additive Reaction Times developed by the author is shown to apply to equilibrium-limited fluid-solid reactions and to be useful in quantitatively analyzing the behavior of such reactions.

## 2:35 PM

**Kinetics of Gaseous Reduction of Mn<sub>3</sub>O<sub>4</sub>:** *Rodney J. Ishak*<sup>1</sup>; Tor Lindstad<sup>2</sup>; <sup>1</sup>Norwegian University of Science and Technology, Matls. Tech. & Electrochem., Alfred Getz vei 2, Trondheim N-7465 Norway; <sup>2</sup>SINTEF, Matls. Tech., Alfred Getz vei 2, Trondheim N-7465 Norway

The reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO has been investigated in a thermobalance apparatus. The charge was composed of manganese ore, decomposed by heating to mainly Mn<sub>3</sub>O<sub>4</sub> and coke. The material was charged to a crucible, which was suspended in the balance. 100% CO-gas was distributed through a grid in the bottom of the crucible.

Two sizes of ores were used; 2,4-4,8 mm and 6,7-9,5 mm. Coke particles was in the size range 4,8-6,7 mm. Experiments were conducted in the 900-1100°C temperature range. The composition of the product gas was monitored continuously. External mass transport between bulk gas and particle surface does not seem to limit the rate of reduction. Assuming that both diffusion through product layer and chemical reaction at the interface between MnO and Mn<sub>3</sub>O<sub>4</sub> are rate controlling the date was tried both in a shrinking core model and in a grain model using regression. The grain model gives the best physical description of the process, because the reactant is a porous media. With this model the effective diffusivity was calculated to be in the 1,5-4·10<sup>-5</sup> m<sup>2</sup>/s range. Pore size was mainly between 0,1 and 10 μm.

## 3:00 PM

**Reaction Kinetics of Some Carbonaceous Materials with Carbon Dioxide:** *M. Kawakami*<sup>1</sup>; T. Ohyabu<sup>1</sup>; T. Takenaka<sup>1</sup>; S. Yokoyama<sup>1</sup>; <sup>1</sup>Toyohashi University of Technology, Dept. Production Sys. Eng., Tempakucho-aza-Hibarigaoka 1-1, Toyohashi 441-8580 Japan

In relation to the designing of new-type blast furnace, the reaction of carbonaceous materials with CO<sub>2</sub> is expected at as low temperature as possible. In order to get a highly reactive carbonaceous material, the reaction kinetics was investigated by measuring such quantities as the reaction rate from weight loss, the amount of CO adsorption and specific surface area by BET method. The reaction rates were in the order of Bintyo char, metallurgical cokes, graphite and glassy carbon. If the rate was converted to the rate per unit area, however, that of Bintyo char was smaller than that of graphite. Thus, it is suggested that the rate of Bintyo char is influenced by the pore diffusion of CO<sub>2</sub>. The rate had a positive relation with the amount of CO absorption, showing that the rate determining step would be the desorption of CO from the active side on the surface.

## 3:25 PM

**Vapor Pressure Measurements for the FeCl<sub>2</sub>-ZnCl<sub>2</sub> System by the Transpiration Method:** *Sang-Han Son*<sup>1</sup>; Fumitaka Tsukihashi<sup>2</sup>; <sup>1</sup>The University of Tokyo, Matls. Eng., 7-3-1, Hongo, Bunkyo, Tokyo 113-8656 Japan; <sup>2</sup>The University of Tokyo, Grad. Sch. of Frontier Scis., 7-3-1, Hongo, Bunkyo, Tokyo 113-0033 Japan

The vapor pressure of ZnCl<sub>2</sub> in the FeCl<sub>2</sub>-ZnCl<sub>2</sub> system was measured by the transpiration method at 873K and 917K. The vapor pressure data were interpreted to indicate the formation of complex ions in the FeCl<sub>2</sub>-ZnCl<sub>2</sub> melts. It is presumed that the complex molecule FeZnCl<sub>4</sub> as well as FeCl<sub>2</sub> and ZnCl<sub>2</sub> exists in the vapors in equilibrium with molten FeCl<sub>2</sub>-ZnCl<sub>2</sub> mixtures. The activities in the FeCl<sub>2</sub>-ZnCl<sub>2</sub> system are shown a negative deviation from Raoult's law. On the basis of those data, thermodynamic properties for the FeCl<sub>2</sub>-ZnCl<sub>2</sub> system were discussed.

## 3:50 PM Break

## 4:10 PM Invited

**The Kinetics of the Oxidation of Zinc Vapour by Carbon Dioxide and Water Vapour on Quartz, Zinc Oxide, Sinter and Coke Substrates:** Antony Cox<sup>1</sup>; *Derek J. Fray*<sup>1</sup>; <sup>1</sup>University of Cambridge, Matls. Sci. & Metall., Pembroke St., Cambridge CB2 3QZ UK

The re-oxidation of zinc vapour in the Imperial Smelting Process is a very important step in the overall process. There have been various studies of the reactions between zinc vapor and oxidising gases and, generally, the same pattern is observed in that at low temperatures a massive deposit is formed whilst at higher temperatures or higher carbon monoxide pressures, a much finer deposit is observed. This work reports new studies on the oxidation of zinc vapour on sinter and carbon so as to reproduce the conditions found in the shaft of the Imperial Smelting Furnace. It was found that the zinc oxide deposited preferentially on coke and sinter rather than on silica. The presence of sulfur resulted in the formation of zinc sulfide on top of the zinc oxide. These observations are discussed in terms of the reactions taking place in the shaft of the zinc blast furnace.

## 4:40 PM

**Effect of P<sub>2</sub>O<sub>5</sub> or Na<sub>2</sub>O Addition on the Reaction Rate of CO<sub>2</sub> Dissociation with Fe<sub>x</sub>O Containing Molten Oxides:** *Hiroyuki Matsuura*<sup>1</sup>; Fumitaka Tsukihashi<sup>1</sup>; <sup>1</sup>The University of Tokyo, Grad. Sch. of Frontier Scis., 7-3-1 Hongo, Bunkyo, Tokyo 113-0033 Japan

The kinetic data of CO-CO<sub>2</sub> reaction with molten oxides are important for the analysis of refining process of metals. The rate constant has been expressed as a function of the composition of ferrous and ferric oxides. The rate constant is affected by the addition of small amount of P<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>O which are a surface active compounds in the molten oxides. In the present work, the reaction rate of CO<sub>2</sub> dissociation on the surface of Fe<sub>x</sub>O-base molten oxides containing P<sub>2</sub>O<sub>5</sub> or Na<sub>2</sub>O was measured by isotope exchange method at 1773K. The effect of P<sub>2</sub>O<sub>5</sub> or Na<sub>2</sub>O addition on the reaction rate was investigated. The rate constant

decreased with increasing  $P_2O_5$  content and the residual rate constant was observed at high  $P_2O_5$  content. The rate controlling step of  $CO_2$  dissociation was discussed.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Monday PM                      Room: Pacific  
March 3, 2003                    Location: San Diego Marriott Hotel

*Session Chairs:* Yasuhiro Awakura, Kyoto University, Dept. of Matls. Sci. & Eng., Kyoto, 606-8501 Japan; Zhang Duomo, Central South University, Metall. Sci. & Eng., Changsha, Hunan 410083 China

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### 2:00 PM Invited

**Preparation of CdS Nanoparticles by Hydrochemical Method and their Surface Modification:** *Zhang Duomo*<sup>1</sup>; Li Qihou<sup>2</sup>; <sup>1</sup>Central South University, Metall. Sci. & Eng., Zuojiang, Changsha, Hunan 410083 China

A novel homogenous precipitation method, including microwave heating, spray feeding, solution conductivity controlling and freeze drying, was developed for the preparation of CdS nanoparticles. The effects of precipitation conditions on the structures and morphologies of CdS particle were discussed. Under the experimental conditions, blende-type CdS was obtained in natrate or sulphate solution, and wurtzite-type CdS was obtained in chloride solution. After solvent-thermal treatment, the amorphous CdS particle, which produced from high concentration solution, turn to double cone or tetrahedron shape. In the precipitation process, the bifunctional thiols of CH<sub>3</sub>CSNH<sub>2</sub> modified the surface of CdS particles and the induced counter ion AOT-SO<sub>3</sub><sup>-</sup> increased the stability and dispersion of CdS particles. The produced particles (4nm to 100nm) can be used to prepare nonlinear optics and self-assemble catalysts.

### 2:35 PM

**Dispersion Characteristics from Two Types of Bubble Generators Commonly Used in Flotation Columns:** *Ramiro G. Escudero*<sup>1</sup>; Francisco J. Tavera<sup>1</sup>; <sup>1</sup>Universidad Michoacana de San Nicolás de Hidalgo, Instituto de Investigaciones Metalúrgicas, Dept. de Metalurgia Extractiva, Santiago Tapia 403, Morelia, Michoacán 58000 México

Over almost forty year has past since the introduction of column flotation. Column technology has grown into several non-mineral applications such as effluents treatment, soils recovery, and de-inking of recycled paper among others. Recent studies have demonstrated that particular characteristics of the dispersion (bubble size, gas holdup, bubble surface area flux), are needed for a given flotation column duty. In this work, two kind of spargers were tested (i.e., internal and external), using a 4 inch column lab, in a two phase system. Results shown the external sparger provides a dispersion with characteristics that include those produced by the two internal spargers.

### 3:00 PM

**Formation Behavior and Corrosion Characteristics of Anodic Films on Mg-Al Alloys in NaOH Solutions:** *Seong-Jong Kim*<sup>1</sup>; Masazumi Okido<sup>1</sup>; Yoshihiro Mizutani<sup>1</sup>; Ryoichi Ichino<sup>1</sup>; Shoji Tanikawa<sup>2</sup>; Saori Hasegawa<sup>2</sup>; <sup>1</sup>Nagoya University, Grad. Sch. of Eng., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan; <sup>2</sup>Nakanihon Die Casting Company, Ltd., Kakamihara 504-0957 Japan

Magnesium is easy to recycle because impurities are easily removed. Recently, there has been great interest in using Mg in automobile parts, mobile personal computers, etc. However, Mg must be surface treated to prevent corrosion, since it is very active. One of the

most efficient surface treatments of Mg is chromate-conversion coating; however, this method causes many problems for the environment, humans, and recycling. Therefore, we studied a non-chromate method of anodizing Mg in NaOH solutions. In this study, the formation behavior and corrosion characteristics of anodic oxide films on pure Mg and Mg-Al alloys were investigated, focusing on the effects of anodizing potential, Al content, temperature, and NaOH concentration. Pure Mg and Mg-Al alloys were anodized for 10 min at 3, 10, 40, and 80 V in NaOH solutions. Mg(OH)<sub>2</sub> was generated by an active dissolution reaction at the specimen's surface, and product was affected by temperature, while MgO generation increased with NaOH concentration. Moreover, the current density after anodizing for 10 min at a constant potential decreased with increasing Al content in Mg-Al alloys.

### 3:25 PM

**Electrochemical Couple Behavior of Manganese Dioxide with Ferrous/Ferric in Acidic Chloride Medium:** *Guo Xueyi*<sup>1</sup>; Li Qihou<sup>2</sup>; Huang Kai<sup>2</sup>; Zhang Duomo<sup>2</sup>; Qiu Dingfan<sup>3</sup>; <sup>1</sup>The University of Tokyo, Ctr. for Collaborative Rsrch., Komaba 4-6-1, Meguro-Ku, Tokyo 153-8505 Japan; <sup>2</sup>Central South of University, Col. of Metallurg. Sci. & Eng., Changsha, Hunan 410083 China; <sup>3</sup>Beijing General Institute of Mining & Metallurgy, Beijing 100044 China

The electrochemical couple behavior of manganese dioxide with ferrous/ferric in acidic chloride medium was investigated. It was found that the dissolution of MnO<sub>2</sub> is due to the electrochemical couple between the MnO<sub>2</sub>/Mn<sup>2+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> in the solution. The driving force for the electrochemical couple reaction originates from their rest potential difference. The reduction of MnO<sub>2</sub> is electrochemically kinetic controlled, whereas the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> is diffusion control. The factors, including the Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cl<sup>-</sup> concentration, pH of the solution, and the temperature, have much influence on the reaction rate of the coupled process. Further, the kinetic equation for the couple reactions was derived in term of Butler-Volmer electrochemical Equations and it was found that the theoretical analysis was quite consistent with the experimental results. This study will be useful to guide the practical leaching of manganese nodule from Deep Ocean and manganese dioxide ore in land.

### 3:50 PM Break

### 4:05 PM Invited

**Electrodeposition of Thin-Layered CdTe Semiconductor from Basic Aqueous Solutions:** *Kuniaki Murase*<sup>1</sup>; Tetsuji Hirato<sup>1</sup>; Yasuhiro Awakura<sup>1</sup>; <sup>1</sup>Kyoto University, Dept. of Matls. Sci. & Eng., Yoshidahommachi, Sakyo-ku, Kyoto 606-8501 Japan

Cadmium telluride (CdTe) semiconductor has been well-investigated for n CdS/p-CdTe heterojunction solar cell material, since its direct band gap of 1.44 eV is suitable for energy conversion from sunlight into electricity. In this talk, a new electrochemical processing of thin-layered CdTe using ammoniacal basic aqueous electrolytes is reviewed. The cathodic electrodeposition of stoichiometric CdTe with a flat and smooth surface morphology took place from the basic electrolytes at potentials positive of the Nernst potential for bulk-Cd deposition and negative of that for bulk-Te. In this potential region, deviation from stoichiometric composition of CdTe electrodeposited was controllable by the Cd(II)/Te(IV) concentration ratio, pH, or concentration of ammonia, a complexing agent, of the electrolytes. These deposition behaviors were well accounted for in terms of potential-pH diagram for the Cd-Te-NH<sub>3</sub>-H<sub>2</sub>O system calculated by a combination of those for Cd-NH<sub>3</sub>-H<sub>2</sub>O and the Te-H<sub>2</sub>O systems.

### 4:40 PM

**Cation Exchange Properties of Zeolites Obtained from Coal Fly Ash by Alkali Hydrothermal Treatment:** *Norihiro Murayama*<sup>1</sup>; <sup>1</sup>Kansai University, Dept. of Cheml. Eng., Fac. of Eng., 3-3-35 Yamatecho, Suitashi, Osaka 564-8680 Japan

Syntheses of zeolitic materials are carried out from coal fly ash by alkali hydrothermal treatment, as part of the reuse and recycle technologies of coal ash. Cation exchange capacity and acid resistance, which are very important in the practical use of cation exchanger in aqueous solution, are measured for the reaction products obtained from coal fly ash. Cation exchange properties of the reaction products are investigated for various cations such as K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup> and so on. The change in crystallization degree and surface texture are noticed before and after cation exchange operation. From these results, the characteristic and its mechanism of cation exchange are clarified for the various zeolitic materials obtained from coal fly ash.

5:05 PM

**The Morphology and Size Control of Cobalt Particles Produced from Concentrated Aqueous Solution:** Chen Song<sup>1</sup>; Liu Zihong<sup>1</sup>; Ai Kan<sup>1</sup>; <sup>1</sup>Central South University, Sch. of Metall., Yuelunlanlu, Changsha, Hunan 410083 China

Cobalt basic carbonate particles were precipitated from 1.0mol cobalt nitrate or cobalt sulfate solution with ammonia carbonate. By controlling the zeta-potential of particles and the ionic strength of the solution, the uniform particles with ellipsoid or rod shapes were obtained. During the precipitation process, the interface intensities were diminished to the minimum, and therefore the Oswald aging and secondary nucleation were both inhibited. The morphology and size control by zeta-potential seems to be the result from thermodynamics rather than classic crystalline kinetics. The particle sizes were in the range of 0.3-0.4 micrometer. After thermolysis, the spindle-type Co<sub>3</sub>O<sub>4</sub> particles were produced. The morphologies of Co<sub>3</sub>O<sub>4</sub> particles were similar to that of their precursors.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: General I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Monday PM Room: Point Loma  
March 3, 2003 Location: San Diego Marriott Hotel

*Session Chairs:* G. A. (Tony) Eltringham, BHP Billiton, Houston, TX 77056 USA; Takahiko Okura, Nikko Techno Service Company Ltd., Tokyo 105-0001 Japan

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### 2:00 PM Keynote

**Production of Elemental Sulphur from Non-Ferrous Smelter Gas:** Takahiko Okura<sup>1</sup>; <sup>1</sup>Nikko Techno Service Company, Ltd., 10-1 Toranomon 2 Chome, Tokyo 105-0001 Japan

Most of non-ferrous raw materials are associated with sulphur. To extract the metals, the sulphur is recovered, typically as sulphuric acid and liquid SO<sub>2</sub>. On the other hand, natural gas may contain over 20% of hydrogen sulphide (H<sub>2</sub>S) and a huge quantity of elemental sulphur is produced together with oil refining in the world. A large fraction of the sulphur mined with natural resources is eventually returned to the earth as fertilizers, by-products of desulphurisation and neutralisation processes, or as fugitives to the atmosphere. However, the supply and demand for the sulphur is in the imbalance. Such situation urges to develop a new smelting process without sulphuric acid production. In this paper, the global sulphur balance and the technologies that recover the elemental sulphur are briefly reviewed. The core of the paper is a proposal to convert SO<sub>2</sub> gas to the elemental sulphur form using organic materials. Some results of thermodynamic calculation and experiments will be presented.

### 2:35 PM Invited

**Physical Chemistry of Reactive Ball Milling:** Geoffrey Alan Brooks<sup>1</sup>; <sup>1</sup>McMaster University, Dept. of Matls. Sci. & Eng., 1280 Main St. W., Hamilton, Ontario L8S 4L7 Canada

Reactive ball milling has been proposed as a new route for producing carbides from oxides through carbothermic reduction. It is claimed that through milling oxide and graphite powders to the nanoscale, amorphous materials with very high reactivity are formed, that allows for easy transformation of the starting material to another in a subsequent thermal process. This paper will examine the thermodynamics of these proposed routes, particularly the effect of scale and localised temperatures on the stability of phases. Methods for calculating the effect of particle size on chemical stability will be described and prob-

lems associated with distinguishing kinetic and thermodynamic effects in these processes will be discussed.

### 3:05 PM

**Investigation in Different Reducing Agents for the Pyro-Metallurgical Treatment of Steel Mill Dusts:** Jürgen Antrekowitsch<sup>1</sup>; <sup>1</sup>University of Leoben, Dept. of Nonferrous Metall., Franz-Josef-Straße 18, Leoben 8700 Austria

Nowadays nearly the half of the world's zinc production are used for galvanizing. Most of the galvanized products return after their life span as scrap to the steel mill. During the steel process the zinc is collected in the flue dust. It is astonishing, that between 40 and 50% of the zinc produced are brought into the steel processing cycle by coated scrap, while only 3 to 5% of the zinc production can be covered by the recycling of the zinc-bearing steel mill dusts. Responsible for this worse ratio is the fact, that established recycling technologies suffer from high energy consumption, low zinc yields, halogen problems and hardly any iron recovery. A development of new, or an optimization of current recycling procedures for the dusts is unalterable because of increasing zinc amounts in these residues and rising costs for the disposal. Different pyrometallurgical recycling technologies are tested in rotary kilns and vertical retorts at the Department of Nonferrous Metallurgy, University of Leoben, Austria. Various reducing agents from carbon monoxide to hydrogen and combinations are used. The results should make it possible to draw conclusions that allow an economical and ecological judgement of the different varieties. The goal is to support the affected industry to increase the low recycling rate and prevent a loss of high zinc values in the steel industry filter dusts.

### 3:30 PM

**On the Behavior of Arsenopyrite in the Process of Roasting:** V. A. Luganov<sup>1</sup>; <sup>1</sup>The K.I. Satpaev Kazak National Technical University, 22 Satpaev str., Almaty 480013 Kazakhstan

Behavior of arsenopyrite under heating was studied by many scientists. It was established that under heating at more than 650°C without air access arsenopyrite dissociates with formation of one atom arsenic. Under vacuum the dissociation process begins at 550°C with formation of elemental arsenic too. The residue of dissociation process contains pyrrhotite and thioilite. In the presence of pyrite arsenopyrite dissociates under lower temperature and with higher velocity than without it. Industrial realization of full scale processing of arsenic bearing raw materials is possible only with the use of standard equipment and oxygen containing blast. In this connection the paper presents the results of the study of the influence of oxygen in the gaseous phase and addition into the charge of pyrite on the process of arsenopyrite decomposition. Thermodynamic analyses has shown that under thermal processing of arsenopyrite in the presence of pyrite and limited quantities of oxygen in the gaseous phase formation of arsenic sulfides is possible according to the following reactions:  
$$\text{FeAsS} + \text{FeS}_2 = 2\text{FeS} + 0.25\text{As}_4\text{S}_4 \quad (1)$$
$$\text{FeAsS} + 0.75\text{FeS}_2 + 2.8125\text{O}_2 = 0.875\text{Fe}_2\text{O}_3 + 0.25\text{As}_4\text{S}_4 + 1.5\text{SO}_2 \quad (2)$$
Other mechanism of reaction also possible. For example:  $\text{FeAsS} + 0.5\text{FeS}_2 + 2\text{O}_2 = 0.5\text{Fe}_3\text{O}_4 + 0.25\text{As}_4\text{S}_4 + \text{SO}_2$  (3). Thermogravimetric and technological investigations of the process have shown: - in the process of thermal processing there is no decrepitation of arsenopyrite particles; - the specific surface and the porosity of dissociating arsenopyrite particles changes extremely with a maximum depending on dissociation degree; - addition of pyrite into the charge decreases diffusional limitation of the process; - the presence of limited quantities of oxygen in the gaseous phase also decreases diffusional resistance of the process; - the main products of arsenopyrite dissociation in the presence of pyrite and oxygen are arsenic sulfides, pyrrhotite and magnetite; - consecutive dosage (addition by parts) of pyrite makes it possible to increase the degree of arsenic sublimation and to obtain cinder with high sulfur pyrrhotite. The technological investigations have confirmed the results of thermodynamical calculations and kinetic research. Chemical, x-ray, electron microscopic analysis and the BET method were used in the course of the investigations.

### 3:55 PM Break

### 4:05 PM Keynote

**The Contribution of Pyrometallurgy to Sustainable Development:** W. J. Rankin<sup>1</sup>; <sup>1</sup>CSIRO Minerals, Bayview Ave., Clayton 3169 Australia

The fundamental issue facing the world is achieving continued economic growth with social equity within the natural limits of the Earth's eco-systems. The basic material and energy needs of the world cannot be met with current ways of addressing these! The demand for

metals will continue into the future because their unique properties make substitution by other materials impossible in many applications and this demand will continue to be met from primary metal production and recycling. However, the recycling rate will increase and the usage pattern of metals will change to reflect the environmental impact of their production and use. In the overall supply chain of material needs, resource processing is a critical stage for the potential release of gaseous, liquid and solid emissions since it is in the processing stage that ores are most physically and chemically transformed. Pyrometallurgy has an important role in meeting the metal needs of the future since some metals can really only be produced pyrometallurgically; the energy required to produce some metals pyrometallurgically is often significantly less than by other methods; most metals are most efficiently recycled pyrometallurgically; and the release of harmful and toxic elements into the biosphere can often best be controlled through pyrometallurgical processing. The development of strategies for pyrometallurgical processing for the future lies in the recognition that sustainable development calls for large step improvements in value delivered per net unit of environmental impact over the entire supply chain. Pyrometallurgy will need to respond to this challenge by contributing to reducing the environmental impact of meeting metal needs using three broad strategies: "end-of-pipe" approaches to convert emissions into benign materials for storage or disposal; flowsheet redesign to limit or eliminate emission production; and improved recycling technologies. A number of examples are discussed to illustrate how the sustainability driver is already influencing the technological development of pyrometallurgical processes and how these will develop further as the sustainability driver strengthens.

#### 4:40 PM Invited

**Some Challenges on Nitride Metallurgy: Synthesis of Complex Nitrides, Phase Equilibria and Chemical Potential Measurements:** *Toru H. Okabe*<sup>1</sup>; *Osamu Ishiyama*<sup>2</sup>; *Hisanori Yamane*<sup>3</sup>; *K. T. Jacob*<sup>4</sup>; *Yoshio Waseda*<sup>3</sup>; <sup>1</sup>The University of Tokyo, Inst. of Indust. Sci., 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan; <sup>2</sup>Nippon Steel Corporation, 6-3 Otemachi 2-Chome, Chiyoda-ku, Tokyo 100-8071 Japan; <sup>3</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls. (IMRAM), 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan; <sup>4</sup>Indian Institute of Science, Dept. of Metall., Bangalore 560 012 India

As part of a systematic study on the thermodynamic properties of complex nitrides, phase equilibria of the system Li-M-N (M = Mg, Al, Ga) at 900 K were investigated. An attempt to determine the thermodynamic properties of complex nitrides was made by using the galvanic cell method, which utilizes LiMgN as an electrolyte under nitrogen atmosphere. The electromotive force (Emf) of the cell at temperatures between 800 and 1100 K was measured. While the Emf of the cell at 900 K was measured to be 0.137 V, data discrepancies of  $\pm 0.03$  V were found. It was difficult to determine temperature dependence of the Emf. The Gibbs energy change for the reaction,  $1/3 \text{Li}_3\text{N} (\text{s}) + 1/3 \text{Mg}_3\text{N}_2 (\text{s}) = \text{LiMgN} (\text{s})$ , at 900 K was determined to be  $\Delta G_o^\circ (\text{LiMgN}) = -13.2 (\pm 2.9) \text{ kJ/mol}$ . Using thermodynamic information on the binary nitride from literature, the standard Gibbs energy of LiMgN was derived to be  $\Delta G_o^\circ (\text{LiMgN}) = -121 \text{ kJ}$  at 900 K. The thermodynamic stability range of nitride was discussed by constructing isothermal chemical potential diagrams that provide a better understanding of the stability region of the LiMgN phase. This diagram was found to be in good agreement with the isothermal phase diagram determined by the alloy equilibration method. Although the obtained data includes large uncertainties, the results provide a better understanding of the thermodynamic stability of nitrides. The potential application of this complex nitride to nitrogen chemical sensors or a medium for controlling nitrogen potential is also shown.

#### 5:10 PM

**Processing of Antimony Raw Materials in Matte Melts:** *O. N. Mustyatsa*<sup>1</sup>; *V. A. Lata*<sup>1</sup>; <sup>1</sup>Kazakh Academy of Sciences, Inst. of Metall., Almati Kazakhstan

Increase in total raw materials balance of antimony production of the share of oxide materials causes the necessity of the development of the new technological schemes for this kind of raw materials, because metal extraction in accordance with the existing technologies is not possible to consider as completely satisfactory. The authors have offered the technology of antimony raw materials processing for metal in one unit by the method of reducing electromelting with production of matte melts and further electrolysis of them. The method of processing includes: -electromelting together with the sodium sulphate and coal with production of the melt of thiosalts and glass melt; - electrolytical isolation of metals from the melts of their thiosalts. Dependencies of antimony extraction from time, temperature, and components ratio have been studied. Kinetic dependency of the contents of admixtures of iron, arsenic, lead and tin in crude metal under

various temperature regimes of reducing melts has been defined. It has been shown that increase of temperature, duration of melting leads to accumulation of iron in antimony. For the production of antimony with low contents of iron the maintenance of optimal conditions (with 800-900C, time of melting 20-30 minutes) is necessary. Maximal antimony extraction has been reached under period of time of electrolysis equal to 1.5 hours and was of the order 99.3%. Investigations made show that electromelting of antimony raw materials to thiosalts with further processing of their melt in the electrolyzer to antimony and sulphur is the base of the new electrochemical technology of wasteless processing of antimony raw materials.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Recycling, Waste Treatment and Environmental Issues I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C5 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Monday PM Room: Leucadia  
March 3, 2003 Location: San Diego Marriott Hotel

*Session Chairs:* Nickolas J. Themelis, Columbia University, Earth & Environl. Eng., New York, NY 10027 USA; M. A. Reuter, Delft University of Technology, Dept. of Appl. Earth Scis., Delft 2628 RX The Netherlands

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#### 2:00 PM Keynote

**Thermal Plasma Treatment of Metal and Material Wastes:** *Patrick R. Taylor*<sup>1</sup>; *Wenming Wang*<sup>1</sup>; <sup>1</sup>Colorado School of Mines, Dept. of Metallurgl. & Matls. Eng., Golden, CO 80401-1887 USA

In the search for the development of a more "environmentally friendly" and more intensive waste disposal approach to meet more and more stringent environmental regulations, thermal plasma-based processes are considered one of the most promising alternatives to the well-established technologies such as incineration. This paper presents an overview on the research and development status of thermal plasma-based waste remediation technologies. The properties of thermal plasma are described. Due to its unique feature of high-energy intensity and super high temperature, thermal plasma is particularly capable of destroying organic-containing wastes. Its potential and promising application areas to the waste remediation may include: treatment of incinerator ashes; metallurgical dusts (especially, electric arc furnace-dust); medical wastes; radioactive wastes; and other Resource Conservation and Recovery Act (RCRA) listed hazardous wastes. Many research institutes and vendors have been involved in the development of the thermal plasma-based waste treatment technology encouraged by the cleanup programs supported by the Environmental Protection Agency (EPA), the Department of Energy (DoE) and the Department of Defense (DoD). More recently, thermal plasma-based waste treatment technologies (sometimes called plasma-enhanced pyrolysis) are focused more and more on not only just destroying organic wastes but also on how to practically, and economically recover energy contained in the organic waste materials in addition to the recovery of metals in order to offset the high operating costs.

#### 2:35 PM

**Modeling of Arsenic Distribution Between Slags and Copper Mattes or Liquid Copper:** *Jonkion M. Font*<sup>1</sup>; *Ramana G. Reddy*<sup>1</sup>; <sup>1</sup>The University of Alabama, Dept. of Metallurgl. & Matls. Eng., PO Box 870202, Tuscaloosa, AL 35487-0202 USA

The present study was undertaken in an attempt to develop a model that can predict a-priori the behavior of arsenic in a slag system. The arsenic capacity based on the Reddy-Blander model was derived for the acidic and basic melts of the hypothetically FeO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub>,

MgO-SiO<sub>2</sub>, FeO-CaO-SiO<sub>2</sub>, FeO-CaO-MgO and FeO-CaO-MgO-SiO<sub>2</sub> systems. The obtained results are summarized as: the arsenic distribution ratio for the hypothetically FeO-CaO-MgO-SiO<sub>2</sub> quaternary system was calculated at 1573, 1523 and 1473 K. Furthermore, the a-priori arsenic distribution ratios were found to be in good agreement with the reported experimental data, when the derived  $\Delta G$  from the experimental data was considered. These results suggest that, the a-priori arsenic distribution model developed here can be used for prediction in a wide range of the FeO-CaO-MgO-SiO<sub>2</sub> slag, matte grade, temperature and pSO<sub>2</sub>. Such predictions will be very useful for understanding the behavior of arsenic in the current and eventually future non-ferrous processes.

### 3:00 PM Invited

**Pyrometallurgical Reactors-Closers of the Recycling Material Cycle:** M. A. Reuter<sup>1</sup>; A. van Schaik<sup>1</sup>; <sup>1</sup>Delft University of Technology, Dept. of Appl. Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

Modern consumer society is governed by the extensive use of complex multi-component products, of which passenger vehicles are an outstanding example. At the end-of-life these products return, as complex multi-component materials that cannot directly be converted into products once more. However society requires that a maximum of end-of-life products find their way back into the industrial and consumer cycle to ensure sustainable development. In order to capture the influence of rapidly changing design of products on recycling, a dynamic optimisation model has been developed that links product characteristics to the optimal recovery of metal in pyrometallurgical reactors. This model consists of a dynamic part, which imbeds an optimisation model. Whereas the dynamic model predicts the behaviour of the resource cycle over time based on various characteristic distribution functions for the changing lifetime, weight and composition of the car, the optimisation model optimises the recycling of the car as a function of product design, efficiency of the different process steps in recycling (i.e. physical separation and pyrometallurgical metal production), economics and legislation. Therefore, it is argued in this paper that the fundamental thermodynamics and kinetics in the metallurgical reactors play a final crucial role in closing the material cycle. Therefore, based on various fundamental simulations, the interaction between the time dependent variables in product design and the optimisation of the recycling of end-of-life vehicles will be discussed in relationship to the fundamental thermodynamics in metallurgical reactors. This implies that central to the discussion is the feedforward control of the feed to the reactors, their composition and the effect thereof on the performance of the reactor and the quality of the produced metal product. The discussed model has been developed in Matlab.

### 3:30 PM

**Thermodynamics of Iron Reduction from Metallurgical Residues:** Ivan Imris<sup>1</sup>; Alexandra Klenovcanova<sup>1</sup>; Matej Imris<sup>2</sup>; <sup>1</sup>Technical University of Kocice, Dept. of Power Eng., Fac. of Mechl. Eng., Letna 9, Kosice 041 87 Slovak Republic; <sup>2</sup>Technical University of Kosice, Dept. of Non-Ferrous Metals & Waste Treatment, Letna 9, Kosice 041 87 Slovak Republic

The iron and nickel production in Slovakia generated many tonnes of very fine residues with iron contents vary from 44 to 74 wt.%. In addition the steelmaking dust contains zinc and lead which are prevented inplant recycling. These kind of residues are usually dumping beside the metallurgical plants to make the environmental problems. Therefore the metal recovery from metallurgical residues has become major interest not only from the viewpoint of metals recycling but mainly from the viewpoint of environmental land protection. The thermodynamic analyses and laboratory experiments suggested that the metals could be recovered from metallurgical wastes by reduction roasting and by plasma smelting processes. The iron rich pellets with very high metallization may be obtained from metallurgical wastes by reduction roasting process and by plasma smelting process the inert slag and pig iron could be produced. In both cases the iron rich products are suitable for the steel production. During reduction roasting and plasma smelting processes the high volatile zinc and lead metals were removed and enriched as a secondary dust, Zn-Pb concentrate, which is suitable for processing in zinc and lead smelters. Suggested processes are commercially feasible and environmentally friendly without any solid or liquid waste.

### 3:55 PM Break

### 4:10 PM Invited

**Simulation of Transport and Chemical Phenomena in Flash Combustion of Municipal Solid Wastes:** Nickolas J. Themelis<sup>1</sup>; Young Hwan

Kim<sup>1</sup>; <sup>1</sup>Columbia University, Earth & Environl. Eng., 500 W. 120th St., #918, New York, NY 10027 USA

Nearly thirty six million tons of municipal solid wastes (MSW) are combusted annually in over one hundred US Waste-to-Energy (WTE) power plants, thus obviating the use of 1.6 billion gallons of fuel oil. One of the advanced WTE processes is the 1-million ton/y SEMASS facility designed by Energy Answers Corp. and operated by American Ref-Fuel in southeastern Massachusetts. Most of the combustion in the three giant combustion chambers occurs while the injected shredded wastes are in flight, i.e., in flash combustion mode. The velocity, temperature, and concentration profiles in the SEMASS combustion chamber were simulated by representing the combustible fraction of MSW by the simplified formula C<sub>6</sub>H<sub>10</sub>O<sub>4</sub> and using the FLUENT Computerized Fluid Dynamics program to solve the turbulent energy and mass transport equations. The results of this model were used to examine options for increasing the productivity of WTE combustion chambers, such as the effect of oxygen enrichment.

### 4:40 PM

**Thermodynamical Analysis of the Chloridization Reaction in Ash Melting Furnace:** Kokoro Iwasawa<sup>1</sup>; Nan Wang<sup>2</sup>; Shu Yamaguchi<sup>2</sup>; Masafumi Maeda<sup>1</sup>; <sup>1</sup>The University of Tokyo, Inst. of Industl. Sci., 4th Dept., 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan; <sup>2</sup>Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555 Japan

Various kinds of remelting or pelletizing processes of primary bottom ash and fly ash evolved from the incineration of municipal solid wastes, have been proposed for the volume reduction and detoxification of residues. In the latter issues, it is important to know the behavior of heavy metal elements in the pyrometallurgical processes. The purpose of the present study is to investigate the chloridization reaction of heavy metal in the ash treatment processes from thermodynamic view point. The present authors focus attention on the effect of Na<sub>2</sub>SO<sub>4</sub> formation in the ash re-melting furnace. From the evaluation of the Na<sub>2</sub>O activity in the Na<sub>2</sub>O-SiO<sub>2</sub>, Na<sub>2</sub>O-CO<sub>2</sub>, Na<sub>2</sub>O-SO<sub>3</sub>, and Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> systems from reported thermodynamic data, it is found that the Na<sub>2</sub>O activity is prominently low in the Na<sub>2</sub>O-SO<sub>3</sub> system, suggesting that NaCl contained in ashes can work as a chloridizer as the following reaction is favored. 2NaCl + SO<sub>3</sub> + 1/2 O<sub>2</sub> = Na<sub>2</sub>SO<sub>4</sub> + Cl<sub>2</sub>. Further discussion on the reaction between oxides (composed of mainly the Na<sub>2</sub>O-SiO<sub>2</sub> system) and salt systems, which are regarded as the NaCl-Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> quasi-ternary system, has been made using the potential stability diagrams at various temperatures. Because of strong temperature dependency of  $\Delta G^\circ$  for the Na<sub>2</sub>SO<sub>4</sub> formation reaction, Na<sub>2</sub>SO<sub>4</sub> formed at lower temperatures can be decomposed to Na<sub>2</sub>O and SO<sub>3</sub> at higher temperatures by the reaction with SiO<sub>2</sub>. The authors proposed a novel processing of solid wastes based on the present results which utilize the formation and decomposition reactions of Na<sub>2</sub>SO<sub>4</sub>.

### 5:05 PM

**Combustion Modeling of Hazardous Waste Incineration:** Y. Yang<sup>1</sup>; M. Pijnenborg<sup>1</sup>; M. A. Reuter<sup>1</sup>; <sup>1</sup>Delft University of Technology, Dept. of Appl. Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

Hazardous waste has often very complicated chemical compositions in variety of physical forms. It is normally processed in rotary kiln incinerators. Due to large variations in waste types and difficulties in feed characterization, the complex transport processes within the incinerator are not well understood, and the incineration process meets great challenges in a smooth operation, and expects various uncertainties in the process chemistry and emission control. For better understanding of the incineration process, process simulation was conducted by using Computational Fluid-dynamics (CFD) to characterize temperature and species distribution in the incinerator. As the first step, hazardous waste in various forms is converted to a virtual fuel or fuel mixture with more or less equivalent chemical compositions and heating value. Then the simulation of the combustion process of this virtual fuel in an industrial-rotary-kiln waste incinerator was carried out with a combustion model. The distribution of temperature and chemical species especially the remaining CO in the system is investigated. The results give a good indication on the combustion efficiency and emission level (indicated by CO concentration), and influences from various operating and process parameters.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Nickel

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Monday PM                      Room: Santa Rosa  
March 3, 2003                    Location: San Diego Marriott Hotel

*Session Chairs:* T. A. Utigard, University of Toronto, Matls. Sci. & Eng., Toronto, Ontario M5S 3E4 Canada; Anthony (Tony) E.M. Warner, Inco Technical Services Ltd., Mississauga, Ontario L5K 1Z9 Canada

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### 2:00 PM Keynote

**An Overview of the Metallurgy of Nickel-Copper Matte Converting:** *Anthony (Tony) E.M. Warner*<sup>1</sup>; Carlos M. Diaz<sup>2</sup>; <sup>1</sup>Inco Technical Services, Ltd., 2060 Flavelle Blvd., Sheridan Park, Mississauga, Ontario L5K 1Z9 Canada; <sup>2</sup>Metallurgical Consultant, 210 Radley Rd., Mississauga, Ontario L5G 2R7 Canada

Inco, Limited has long and varied experience in converting nickel-copper primary smelting mattes over a broad range of both nickel/copper weight ratios and combined nickel-copper-cobalt contents. In addition, at the Copper Cliff Smelter, the composition of the converter product matte has to meet the requirements of the matte separation process while, at the Thompson Smelter, converter matte with a different composition is cast into anodes for nickel electrowinning. Recently, Inco has conducted pilot plant tests of three possible nickel-copper matte continuous converting routes, namely flash converting, oxygen top blowing-nitrogen bottom stirring, and tuyere blowing. This work has generated substantial new information on nickel-copper matte converting chemistry. In this overview paper, the metallurgy of nickel-copper matte converting is reviewed with emphasis on the behaviour of cobalt and on the operating conditions required to meet the iron and sulfur specifications of the product matte. The available relevant thermodynamic information is used to discuss the industrial data.

**2:30 PM                      Replaced: Please see Addendum, page 39**  
**Miniplant Oxygen Flash Smelting of Bulk Copper-Nickel Sulfide Concentrate: The Effect of Coke Addition on Process Metallurgy:** *Jin Liu*<sup>1</sup>; Anthony E.M. Warner<sup>1</sup>; Torstein Utigard<sup>2</sup>; Carlos M. Diaz<sup>2</sup>; Mustafa Fezzani<sup>1</sup>; <sup>1</sup>Inco Technical Services, Ltd., 2060 Flavelle Blvd., Sheridan Park, Mississauga, Ontario L5K 1Z9 Canada; <sup>2</sup>University of Toronto, Dept. of Matls. Sci. & Eng., 184 College St., Toronto, Ontario M5S 3E4 Canada

At its Copper Cliff Smelter, Inco, Limited processes a bulk copper-nickel concentrate in two Inco oxygen flash furnaces. The furnace matte is converted to low iron matte for further processing, and the molten converter slag is recycled to the flash furnaces. The flash furnace slag is discarded. Natural gas or, in recent years natural gas combined with coke, supplies a minor proportion of the process heat requirements, thus limiting the flash furnace matte grade to the target 45% CuNiCo. Coke addition to the furnace offers a potential means of establishing a reducing barrier on the surface of the molten bath. Such a practice would be conducive to producing sulfur deficient (partially metallized) matte. At the same iron content, the iron activity of sulfur deficient matte is higher than that of regular matte. A supernatant coke barrier could, therefore, be expected to lead to higher nickel and cobalt recoveries, reduction or even elimination of magnetite furnace bottom buildup and increased sulfur elimination as SO<sub>2</sub> in the flash furnace. Preliminary experiments were conducted in a miniplant flash furnace to investigate the feasibility and merits of this process scheme. This paper presents the experimental results and discusses key aspects

of the possible operation of the Inco flash furnace with a coke barrier separating the freeboard from the molten bath.

**2:55 PM                      Replaced: Please see Addendum, page 39**  
**The Operation of the INCO Flash Furnace Uptake: Combustion of H<sub>2</sub>S and Formation of Uptake Buildup:** *Jin Liu*<sup>1</sup>; Anthony E.M. Warner<sup>1</sup>; Geoff Osborne<sup>2</sup>; *Darryl Cooke*<sup>2</sup>; Ralph Slayer<sup>1</sup>; <sup>1</sup>INCO Technical Services, Ltd., 2060 Flavelle Blvd., Sheridan Park, Mississauga, Ontario L5K 1Z9 Canada; <sup>2</sup>INCO, Ltd., Copper Cliff Smelter Techn. Services, Copper Cliff, Ontario P0M 1N0 Canada

The 15m high INCO flash furnace uptake was designed as a reaction chamber with the objective of destroying the H<sub>2</sub>S contained in the furnace off-gas by combustion with oxygen at about 1300°C. Until recently, the oxygen required for this purpose was injected through afterburners located at the bottom of the uptake. An undesirable side effect of this practice was the formation of build up accretions on the inside walls of the uptake. This buildup had a negative impact on both the furnace on line time and the control of the flash smelting process. In late 2001, the afterburners were relocated to the roof of the uptake. As a result, about 80% of the uptake accretion buildup disappeared with obvious beneficial effects for the operation of the furnace. This paper discusses key flash smelting aspects that affect the operation of the flash furnace uptake such as the dusting rate, the formation of H<sub>2</sub>S in the freeboard of the furnace, and the impact of using coke to supply some of the heat required by the process. The mechanism of buildup formation and its dependence on uptake afterburners location are also examined. Prof. Yazawa's sulfide smelting thermodynamic relationships proved instrumental in understanding the conditions that influence the formation and the elimination of H<sub>2</sub>S and uptake buildup.

**3:20 PM**  
**Nickel and Copper Behaviour in the Process of Autogenous Smelting of the Concentrate after High-Grade Matte Separation:** *L. Sh. Tsemekhman*<sup>1</sup>; A. G. Ryabko<sup>1</sup>; L. B. Tsymbulov<sup>1</sup>; G. P. Miroevskiy<sup>1</sup>; A. N. Golov<sup>1</sup>; <sup>1</sup>AO "Gipronickel", 1 Grazhdansky Pr., Saint-Petersburg 195220 Russia

At Severonickel Combine JS the process of autogenous smelting of copper concentrate after high-grade matte separation in a stationary unit with upper oxygen blow is being brought to a commercial level. Due to heat deficit fuel oil is put on together with the blow. Processes for autogenous smelting of the concentrate with crude blister and blister copper and liquid silicon slag have been developed and tested. Ni:Cu ratio in the slag is higher than in solid slag, formed in crude blister copper converting. Conduct of Ni, Cu and Co forms of metals in slag as well as gas mode of the -process have been studied.

**3:45 PM Break**

**3:55 PM Invited**  
**Laboratory One-Step Bath Smelting of Nickel Concentrate to a Low Iron Matte:** *N. J. Tamnyan*<sup>1</sup>; T. A. Utigard<sup>1</sup>; <sup>1</sup>University of Toronto, Matls. Sci. & Eng., Toronto, Ontario M5S 3E4 Canada

Laboratory bath smelting tests were conducted to determine the feasibility of smelting nickel-copper concentrate directly to a low iron matte in one step. Concentrate, air/oxygen and a silica flux were fed to a matte-slag bath kept in MgO crucibles at 1300°C. Various oxygen enrichments and smelting rates were used to maintain 0.5 to 2 wt% iron in the product matte. The slag losses are comparable to those obtain under similar industrial conditions. Due to the highly oxidizing conditions required to produce mattes with low iron contents, it is not recommended to target iron contents below about 2% in the matte. The specific bath smelting rates were equal to or higher than those in various industrial bath smelting processes.

**4:20 PM                      Replaced: Please see Addendum, page 39**  
**Improving the Operating, Maintenance and Repair Practices of an Inco Flash Furnace at the Copper Cliff Smelter:** *Randy Lawson*<sup>1</sup>; W. Peter Lee<sup>2</sup>; <sup>1</sup>Copper Cliff Smelter Complex, Copper Cliff, Ontario P0M 1N0 Canada; <sup>2</sup>Inco Technical Services, Ltd., 2060 Flavelle Blvd., Mississauga, Ontario L5K 1Z9 Canada

Inco's Copper Cliff Smelter in Sudbury, Ontario operates two (2) Inco flash smelting furnaces treating a copper-nickel (bulk) concentrate produced by the area's milling operations. Daily concentrate throughput averages ~4800 tonnes at a grade ~21% CuNiCo by mass. The two new flash furnaces began the bulk smelting operation around 1993 as part of the Inco's SO<sub>2</sub> abatement project. Over the years, a number of specialized repair procedures have been developed with the intention of increasing on-line time, productivity and longevity (vessel integrity) between major turn-arounds. Some of the more significant improvements and repair procedures are highlighted in this paper with the aim of providing other furnace operators some ideas for development of their respective technologies.

4:45 PM

**Direct Sulfation of Nickel Laterite Ores Using SO<sub>2</sub>-Rich Gases:** D. Papazoglou<sup>1</sup>; W. J. Rankin<sup>2</sup>; <sup>1</sup>WMC, Ltd., Kwinana Nickel Refinery, Kwinana, WA 6167 Australia; <sup>2</sup>CSIRO Minerals, Clayton, VIC 3169 Australia

This work was undertaken to investigate the thermodynamic and kinetic feasibility of using hot sulfur dioxide bearing gases from smelting processes to selectively sulfate the nickel in nickel laterite ores for subsequent extraction in water. The environmental benefits of this approach, as opposed to releasing the gas to the atmosphere, and the economic benefit of directly utilising the SO<sub>2</sub> rather than converting it to sulfuric acid are strong drivers for such a process. A thermodynamic analysis indicated that selective sulfation of the nickel could be feasible under certain conditions and these were explored through a series of laboratory scale experiments. Laterite samples were reacted at temperatures between 500 and 800°C with an equilibrated mixture of sulphur dioxide, oxygen and nitrogen in a fixed bed reactor. Tests were conducted on saprolitic ore from Bulong, Western Australia, limonitic ore from New Caledonia and garnieritic ore from Indonesia. The main variables examined were reaction temperature, st length of the sulphating atmosphere, reaction time and particle size. Nickel extractions were highest from the limonite and relatively low from the other ores. The maximum selective extraction of nickel from the limonite in a single step sulfation was 73%. A two-step process was also identified which involved removing the reaction products by leaching and then sulphating again at the same conditions. This increased the extraction for the limonite ore to around 84% Ni, 95% Co and 2% Fe. Extraction from the garnierite ore was strongly dependent on particle size. The 106-212 mm fraction yielded only 15% Ni extraction, in a single step sulfation, whereas the <30 mm fraction yielded 66%. In contrast, the limonite ore showed an increase from 72% to 74% Ni extraction over the same range. Maximum nickel extractions from the saprolite ore were generally below 60%, but increased to around 70% with the two-step process. Direct sulfation of laterite could be feasible in locations where sulfide smelting or roasting operations are relatively close to laterite deposits. Such a location is in the Kalgoorlie region of Western Australia.

5:10 PM

**An Investigation on the High-Mg-Content Slag in Jinchuan Nickel Flash Smelting:** Wan Zhi<sup>1</sup>; Wan Wei<sup>1</sup>; <sup>1</sup>Jinchuan Non-Ferrous Metals Company, Ltd., Jinchang, Gansu 33000 China

High-Mg-content concentrates are usually treated in Jinchuan flash smelting furnace. Because the viscosity of high-Mg-content slag is very high, the operation of flash smelting becomes very difficult. After adjusting the ratio of FeO/SiO<sub>2</sub> and operation conditions, the flash smelter works smoothly. The nickel content in the slag can decrease to 0.18-0.22%.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Metals and Sulfide Systems

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM                      Room: Solana  
March 4, 2003                      Location: San Diego Marriott Hotel

*Session Chairs:* R. Hurman Eric, University of the Witwatersrand, Sch. of Process & Matls. Eng., Wits 2050 S. Africa; Seshadri Seetharaman, Royal Institute of Technology, Div. of Metall., Stockholm SE-100 44 Sweden

8:30 AM Keynote

**Solute Interactions with Dissolved Oxygen in Molten Copper Systems:** Seshadri Seetharaman<sup>1</sup>; Patrik Fredriksson<sup>1</sup>; Ragnhild Aune<sup>1</sup>;

<sup>1</sup>Royal Institute of Technology, Div. of Metall., Stockholm SE-100 44 Sweden

In fire refining of copper, the affinities of various impurity elements on dissolved oxygen is of great significance. Further, in the design of oxygen probes in liquid copper, the influence of solute interactions on the activity of oxygen need to be considered in order to evaluate the oxygen concentration in molten copper. The present paper presents a series of measurements of the activities of oxygen in liquid Cu-M-O alloys (where M stands for Mn, Zn, As, Se or Te) carried out by the present group employing the solid electrolyte galvanic cell technique. Extreme care was taken to control the oxygen potentials in the inert gas atmosphere, and to keep the oxygen levels very low in the molten metal. The oxygen content was determined by analysis of the samples taken out from the melt. The results obtained showed that Mn has a strong negative influence on the activity coefficient of oxygen in liquid copper. A similar, but less prominent effect was observed in the case of Zn. Arsenic had no influence on the activity of oxygen in Cu (liq.). Se and Te had slight negative effect on oxygen activities in copper at X<sub>O</sub>10<sup>-5</sup>, while at lower oxygen levels the interaction coefficients were found to be positive. The results obtained were compared with empirical models for the calculation of interaction coefficients available in literature.

9:05 AM

**Desulfurization Kinetics of Molten Copper Matte by Gas Bubbling:**

H. Sang Sohn<sup>2</sup>; Yasuhiro Fukunaka<sup>1</sup>; Toshio Oishi<sup>3</sup>; <sup>1</sup>Kyoto University, Dept. of Energy Sci. & Tech., Sakyo-ku, Kyoto 606-8501 Japan; <sup>2</sup>Kyungpook National University, Dept. of Matls., Daegu 702-701 Korea; <sup>3</sup>Kansai University, Dept. of Matls. Eng., Suita 564-8180 Japan

The kinetic study on desulfurization of copper matte by gas bubbling was designed under the presumptions of lower FeO activity and of no fayalite slag formation. Copper matte with 59% Cu and 22.6% S in weight ratio was oxidized at 1523K by bubbling of Ar+O<sub>2</sub> gas through a submerged nozzle. The effects of oxygen partial pressure and flow rate of gas on the oxidation rate of matte were discussed. The desulfurization rate and evolution rate of SO<sub>2</sub> gas of copper matte were influenced by the oxygen partial pressure. However, they were confounded each other. The desulfurization rate and evolution rate of SO<sub>2</sub> gas of copper matte were described by the mass transfer rate through the gas film around the rising gas bubbles. The calculated results reasonably describe the observed desulfurization rate and evolution rates of SO<sub>2</sub> gas at a constant oxygen partial pressure of 0.2 atm.

9:30 AM

**Phase Equilibria and Thermodynamics in the Ag-Pb-S Ternary System:**

R. Hurman Eric<sup>1</sup>; Hakan Ozok<sup>1</sup>; <sup>1</sup>University of the Witwatersrand, Sch. of Proc. & Matls. Eng., PB 3, Wits, Johannesburg, Gauteng 2050 S. Africa

Within the Ag-Pb-S ternary system, the boundaries of the immiscibility region together with the tie-line distributions were re-established at 1198K by the equilibration-quenching technique where samples were kept in evacuated and sealed silica capsules. Activities of Pb were measured by the dew-point method along the Ag-Pb binary at 1198, 1373 and 1473K. Positive deviations were observed and the results were modelled by the Krupkowski formalism. Activities of Ag, Pb, and S, along the ternary miscibility gap were calculated at 1198K by utilizing the bounding binary thermodynamics, phase equilibria and tie-lines. Activities of Pb were also measured along the metal-rich boundary of the miscibility gap to confirm the calculated Pb activities at 1198K.

9:55 AM

**Activities of the Cu<sub>2</sub>S-FeS System Calculated from the Data of the**

**Cu<sub>2</sub>S-FeS-Sb<sub>2</sub>S<sub>3</sub> System:** Grigore Matei<sup>1</sup>; Yasushi Takasaki<sup>2</sup>; Kimio Itagaki<sup>3</sup>; Kazuo Koike<sup>2</sup>; <sup>1</sup>University "Politehnica" of Bucharest, Matls. Sci. & Eng. Fac., Spl. Independentei 313, Bucharest Romania; <sup>2</sup>Akita University, 1-1 Gakuen-Cho, Tegata, Akita 010-8502 Japan; <sup>3</sup>Tohoku University, 2-1-1 Katahira, Aoba-Ku, Sendai 980-8577 Japan

The thermodynamic property of the Cu<sub>2</sub>S-FeS system is important not only in the case of copper smelting but also in the case of general pyro-metallurgy. However, there are not many reported activity data. In this study, activities of Cu<sub>2</sub>S and FeS in the Cu<sub>2</sub>S-FeS system were calculated using the Darken's method from the activity data of the Cu<sub>2</sub>S-FeS-Sb<sub>2</sub>S<sub>3</sub> system measured by the transportation method at 1050°C. The activities of Cu<sub>2</sub>S and FeS in the Cu<sub>2</sub>S-FeS system showed negative deviation from the ideal behavior and satisfied the relation of the Gibbs-Duhem equation.

## 10:20 AM Break

### 10:40 AM Invited

**High Temperature Thermodynamic Studies on Sulfide Systems Using the Dew Point Technique:** *R. Hurman Eric*<sup>1</sup>; <sup>1</sup>University of the Witwatersrand, Sch. of Process & Matls. Eng., PB 3, Wits 2050 S. Africa

The dew-point technique of activity measurements take advantage of the volatility of a component in solution. The pressure of the volatile component over a sample is determined from observations of the temperature at which condensation of the vapor occurs. The method is applicable best when the vapor pressure of the components would differ by about two to three orders of magnitude. Experimentally, this is a closed system involving the use of evacuated and sealed transparent quartz sample probes. Furthermore reliable vapor pressure data of the volatile component is essential along with a specialized high temperature furnace capable of giving reproducible results. In this context, the vertical Dew-Point Furnace (DPF) was designed and built after elaborate trials until enough proficiency was gained for reproducible results. Over the years the DPF was modified and improved. The DPF developed was versatile and could easily be used for activity measurements in the isopiestic mode (another method of measuring activities of a volatile component in a solution). The necessary ancillary systems; namely evacuation-flushing-evacuation followed by sealing of quartz sample probes under vacuum were also perfected over the years. As and when necessary the dew-point technique was supplemented by classical equilibration-quenching method employed on sealed quartz sample probes to reveal necessary phase equilibrium information. The following were studied utilizing the above technique: (i)Activities in Cu<sub>2</sub>S-PbS and FeS-PbS binary and Cu<sub>2</sub>S-FeS-PbS ternary at 1200°C, (ii)Phase equilibria and thermodynamics in the Pb-PbS system, (iii)Phase equilibria and thermodynamics in the Cu-Pb-S and Fe-Sn-S systems, (iv)Activities in FeS-SnS and Ag<sub>2</sub>S-SnS binary and FeS-Cu<sub>2</sub>S-SnS ternary at 1200°C,(v)Phase equilibria and thermodynamics in Ag-Pb, Fe-Pb-S, Ag-Sn-S and Ag-Pb-S systems. Most recently the following systems have been tackled: Phase equilibria and thermodynamics in the Sn-Pb-S system and activities in Ag<sub>2</sub>S-PbS binary, Ag<sub>2</sub>S-Cu<sub>2</sub>S-PbS and Ag<sub>2</sub>S-FeS-PbS ternaries and Ag<sub>2</sub>S-Cu<sub>2</sub>S-FeS-PbS quaternary at 1200°C.

### 11:10 AM

**Thermodynamic Properties of Copper-Nickel Mattes:** *L. Sh. Tsemekhman*<sup>1</sup>; A. V. Tarasov<sup>2</sup>; V. M. Paretsky<sup>2</sup>; <sup>1</sup>AO "Gipronickel", 1 Grazhdansky Pr., Saint-Petersburg 195220 Russia; <sup>2</sup>GINTSVETMET", 13 Acad. Korolyov St., Moscow 129515 Russia

Studies into thermodynamic properties of Cu-Ni and Cu-Ni-S systems and mattes have been conducted with the aid of a MC-1301 mass-spectrometer designed for investigation of processes of vapor formation of difficult-to-volatilize substances. The instrument constitutes a combination of an evaporator of Knudsen chamber type and a mass-spectrometric analyzer of vapor phase. Effusion Knudsen chambers were preliminarily calibrated based on the silver and gold vapor pressure recommended as IUPAC pressure standards. Partial pressures of vapor components were determined, depending on the objective set, by the method of complete isothermal evaporation or the ion current comparison method. Measurements of temperature relationship of the ion current intensity of Cu<sup>+</sup> and Ni<sup>+</sup>, as well as atomic copper vapor pressure above molten copper and atomic nickel vapor pressure above solid nickel metal using the method of complete isothermal evaporation made it possible to define equations of the effect of temperature within a range of 1400K to 1800K on copper and nickel vapor pressures. The process of copper-nickel system evaporation within the entire range of compositions had a clear-cut incongruent character and the intensity of ion current of Cu<sup>+</sup> during the test period decreased, while that of Ni<sup>+</sup> increased. When studying the Cu-Ni-S system, the sulfur partial pressure was measured by the complete isothermal evaporation method and the copper and nickel partial pressure was measured by the ion current comparison method. The values of partial pressures of components above the Cu-Ni-S melt were used for calculation of activities of these components in the melt. The copper and nickel activity data were used for assessment of the value of soluble losses of these metals in slag of autogenous smelting. Studies of evaporation processes of commercial-grade mattes were carried out at a temperature of 1500K. As a result of processing of experimental data, relationships of partial pressures of copper, iron and sulfur, % at.: 0.3-15.4 Cu, 35.2-80.6 Fe and 10.4-30.7 Ni. <p>PCu = 1.35 - 0.034[Cu] - 0.013[Fe] - 0.014[Ni] (1) P = 1.52 - 0.039[Cu] - 0.015[Fe] - 0.010[Ni] (2) PFex10-2 = 1.10 - 0.024[Cu] + 0.004[Fe] - 0.039[Ni] (3) <p> Activity values and activity coefficients of nickel have been calculated on the basis of the data obtained.

## 11:35 AM

**Determination of the Degree of Oxidation of Molten Copper Using an Electrochemical Cell:** *José Alberto Vázquez-Monroy*<sup>1</sup>; José Antonio Romero-Serrano<sup>1</sup>; Mario Alberto García-García<sup>1</sup>; Samuel Ganzález López<sup>1</sup>; <sup>1</sup>E.S.I.Q.I.E-IPN, Metallurg. Eng., Unidad Profesional Adolfo Lopez Mateos, Lab. Pesados de Metalurgia, México D.F. 07738 México

Copper is the third most widely used metal in terms of tonnage per year throughout the world, after iron and aluminum. Copper is an excellent conductor of electricity and heat, only slightly exceeded by silver. The electrical conductivity of copper explains its the sharp increase with the arrival of the age of electricity. At the present, almost 75% of copper consumption goes into this type of usage. The high temperature galvanic cells have come into prominence on account of their numerous applications in both fundamental and applied measurements. Since the inception of the oxygen-ion conducting electrolytes like ZrO<sub>2</sub>-CaO, the oxygen concentration cells have been extensively used in laboratories as well as in industries. In metal production technology, these cells have been used to monitor the oxygen potentials in metals. The pioneer among the various industrial users of such cells is the copper industry. Today, high temperature solid electrolyte cells involving oxygen ion conducting electrolytes have become an integral part of copper pyro-refining and continuous casting, because it is possible to control the oxygen level and to predict the amount of other alloy elements. For these reasons, in the present paper the degree of molten copper oxidation was determined in terms of the amount of Cu<sub>3</sub>P used as deoxidant, the particle size of Cu<sub>3</sub>P and temperature. The oxygen sensor was prepared with Zirconia Stabilized with Itria (ZEL), using Ni-NiO as reference electrode. The first part of this study consisted of developing an electrochemical cell to measure the oxygen activity in molten copper. The second part consisted of a thermodynamic analysis, which was carried out with a commercial software FACT (Facility for the Analysis of Chemical Thermodynamics). This software has databases of pure substances and systems in solution and can be used to study complex process like the Copper production. The thermodynamic study allowed to relate the oxygen activity and its concentration. Finally it was developed a model of dissolution of Cu<sub>3</sub>P in the bath in terms of the reaction time and temperature, which allows to estimate the dissolution rate of Cu<sub>3</sub>P particles in the melt.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. NPM/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM  
March 4, 2003

Room: Pacific  
Location: San Diego Marriott Hotel

*Session Chairs:* Yoshiaki Umetsu, Tohoku University, Inst. of Multi. Rsrch. for Adv. Matls., Sendai 980-8577 Japan; Rafael Padilla, University of Concepción, Metallurg. Eng., Concepción Chile

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### 8:30 AM Keynote

**Environmentally Friendly Route to Copper Production: Sulfidation and Leaching of Chalcopyrite Concentrates:** *Rafael Padilla*<sup>1</sup>; <sup>1</sup>University of Concepción, Metallurg. Eng., Edmundo Larenas 270, Concepción Chile

In the production of copper from chalcopyrite (CuFeS<sub>2</sub>) concentrates by the smelting and converting technology, the ambient pollution with gaseous SO<sub>2</sub> and toxic metals such as arsenic compounds is still a serious problem, especially in the converting step due to the batch nature of the conventional Peirce Smith process. Non-SO<sub>2</sub> emitting alternatives are leaching processes. However, few of them have had a limited industrial application and they are not very effective in

discarding safely the toxic impurities. A combination of pyro-hydro-metallurgical methods: the sulfidation of chalcopyrite and subsequent leaching of the sulfidized material is a non-polluting alternative to treat not only clean chalcopyrite concentrates but also complex chalcopyrite-enaigite concentrates. In this article, this alternative is discussed concerning the thermodynamics and kinetics of the sulfidation of chalcopyrite with gaseous sulfur. The kinetics of the leaching of the sulfidized concentrate in an H<sub>2</sub>SO<sub>4</sub>-NaCl-O<sub>2</sub> system is also discussed.

9:05 AM

**Construction of Electrical Conductivity of Copper Sulfate Electrolytes Acidified with Sulfuric Acid for Copper Electrorefining and Electrowinning Processes:** Kazuteru Tozawa<sup>1</sup>; Yoshiaki Umetsu<sup>2</sup>; Qing-Quan Su<sup>3</sup>; Zi-Qiang Li<sup>4</sup>; <sup>1</sup>Tohoku University, Sendai 980-0845 Japan; <sup>2</sup>Tohoku University, Inst. of Multi. Rsch. for Adv. Matls., Sendai 980-8577 Japan; <sup>3</sup>Ebara Corporation, Tokyo 144-8510 Japan; <sup>4</sup>Chandu Science and Technical University, Chandu China

The electrical conductivity of electrolytes for copper electrorefining and electrowinning processes has been reported by many researchers since 1911. The experimental results show that the conductivity increases with an increase in sulfuric acid concentration, but decreases with an increase in copper concentration. In pure copper sulfate solution, however, the conductivity increases with an increase in copper concentration. After confirming the conductivity of pure and acidified copper sulfate solutions experimentally, we found that the conductivity of acidified copper sulfate electrolytes is mainly controlled by concentrations of hydrogen ion and free (not hydrated) water. It can be explained on the basis of the finding that the conductivity of copper sulfate electrolytes acidified with sulfuric acid decreases with an increase in copper concentration.

9:30 AM

**Separation of Copper and Arsenic from Copper-Arsenic-Sulfuric Acid Electrolytes by Using Electrodialysis:** J. P. Ibanez<sup>1</sup>; C. Gutierrez<sup>1</sup>; L. Cifuentes<sup>2</sup>; <sup>1</sup>Arturo Prat University, Dept. of Metall., Av. Arturo Prat 2120, Iquique Chile; <sup>2</sup>Universidad de Chile, Dept. of Mining Eng., Av. Tupper 2069, Santiago Chile

The separation of arsenic and copper from Cu-As-H<sub>2</sub>SO<sub>4</sub> electrolytes by using electrodialysis was investigated at ambient temperature in a laboratory batch cell. The effect of current density and pH were studied. A solution of copper free of arsenic was obtained by this technique at all the conditions investigated. The efficiency for the transport of Cu<sup>2+</sup> was found to reach values higher than 98% in 3 hours. The transport of arsenic and copper through the ion exchange membranes was favored by increasing the pH and by increasing the current density. The pH of the system was found to be a key parameter for the process, since it controls the speciation of the ions to be transported and the formation of unwanted precipitates that reduced the global efficiency of the electrodialysis process. The main conclusion of the work is that the electrodialysis is a promising technique to be used in separating and/or concentrating ions of interest in electrometallurgical plants of copper.

9:55 AM

**Effect of Fe(II), Co(II) on the Formation of Lead and Manganese Oxides During Copper Electrowinning:** A. Pagliero<sup>1</sup>; F. Vergara<sup>1</sup>; J. Ipinza<sup>2</sup>; J. L. Delplanck<sup>3</sup>; <sup>1</sup>University of Concepción, Dept. of Metallurg. Eng., Edmundo Larenas 270, PO Box 53-C, Concepción 00187 Chile; <sup>2</sup>University Arturo Prat, Dept. of Metallurg. Eng., Arturo Prat 2120, PO Box 121, Iquique Chile; <sup>3</sup>University Free of Brussels, Fac. of Appl. Scis., 50 Av. F.D. Roosevelt, CP 194/03, Brussels B-1050 Belgium

Small manganese concentration and other impurities (Fe<sup>2+</sup>, Al<sup>3+</sup>) in the high acid electrolyte are transferred to copper electrowinning. Experimental test of electrolysis were conducted a 50°C in 180 g/L H<sub>2</sub>SO<sub>4</sub> to investigate the behavior of manganese and iron in solution on the film stability of the alloy PbCaSn. The effects of ions such as Fe<sup>2+</sup>, Co<sup>2+</sup> in acidic electrolytes with manganous ions on the anode corrosion were investigated. These impurities were found to affect the anode PbCaSn corrosion. The presence of 4g/L Fe<sup>2+</sup> in the electrolyte and different manganese concentration in the rank 0.07 to 4 g/L, inhibit the formation of slimes formed by β-MnO<sub>2</sub> tetragonal (disproportionation reaction). However, the layer of MnO<sub>2</sub> amorphous formation on the lead oxides is uninterrupted but its thickness is very thin. This condition aid the dissolution of the PbO<sub>2</sub>. The corrosion of PbCaSn anode is much less when it is compared to media containing only cobalt and manganese.

10:20 AM Break

10:35 AM Invited

**Surface Tension, Density and Viscosity Coefficient of Acidic Copper Sulfate Solution Simulating Electrolyte Solution for Electrolytic**

**Copper Production With/Without Addition of Gelatin:** Kazuteru Tozawa<sup>1</sup>; Qing-quan Su<sup>2</sup>; Yoshiaki Umetsu<sup>3</sup>; <sup>1</sup>Tohoku University, Sendai 980-0845 Japan; <sup>2</sup>Ebara Corporation, Tokyo 144-8510 Japan; <sup>3</sup>Tohoku University, Inst. of Multidisciplinary Rsch. for Adv. Matls., 1-1 Katahira 2-chome, Aoba-ku, Sendai 980-8577 Japan

Surface tension, density and viscosity coefficient of the acidic copper sulfate solutions simulating electrolyte solution for copper electrorefining has been measured and are summarized as a function of the solution composition and temperature. Nickel sulfate is taken to be a representative coexisting sulfate affecting the physical properties of the electrolyte solution. The sulfates in the solutions including sulfuric acid increase the values of physical properties under consideration. Gelatin, representing organic additives for electrolyte solution, was found to sensitively affect the surface tension of the solution at low concentration less than 200mg/L. The surface tension was markedly lowered by addition of gelatin and the higher concentration of gelatin led to more pronounced decrease in the measured values. The surface tension gradually increased with time after addition of gelatin and the increment was enhanced by higher acid concentration and higher temperature. The observed change in the surface tension is considered to reflect preferential adsorption of gelatin to the solution surface and decomposition of gelatin due to hydrolysis to form various molecules having smaller molecular weights.

11:05 AM Invited

**The Mechanism of Sphalerite Dissolution in Ferric Sulphate-Sulphuric Acid Media:** A. Pratt<sup>1</sup>; J. E. Dutrizac<sup>1</sup>; T. T. Chen<sup>1</sup>; <sup>1</sup>CANMET, 555 Booth St., Ottawa, Ontario K1A 0G1 Canada

Fracture exposed surfaces of sphalerite samples having five different iron contents ranging from approximately 0 wt% to 14.8 wt% Fe were leached from 15 to 120 seconds at 100°C in 0.3 M Fe(SO<sub>4</sub>)<sub>1.5</sub>-0.3 M H<sub>2</sub>SO<sub>4</sub> media. The reacted samples were examined using X-ray photoelectron spectroscopy (XPS) which provides chemical state information on the first few nanometers of the solid surface. Surface compositions obtained from reference and leached sphalerites show that the leaching rate increases with increasing iron content. Detailed evaluation of high resolution S2p spectra show that the leaching progresses via the formation of polysulphide species. Disulphide species were not detected in any of the experiments. Examination of the Zn2p and Fe2p spectra show little change in the chemical states over the duration of these experiments. Longer leaching times resulted in the generation of elemental sulphur. The ratios of elemental sulphur to dissolved ferrous ions and zinc suggest that less than 5% of the sulphide is oxidized to sulphate, for zinc extractions ranging from 8 to 100%. Morphological studies showed that the elemental sulphur initially formed at a few isolated sites, such as the grain boundaries. Furthermore, faceted euhedral sulphur crystals were often identified. These observations suggest that at least part of the elemental sulphur forms via dissolved sulphide species which are oxidized in solution by the ferric sulphate.

11:35 AM

**Technological Flowsheet of Sulfide Copper Concentrates Treatment as Non-Ferrous Metals Production By-Products:** Y. M. Shneerson<sup>1</sup>; A. Y. Lapin<sup>1</sup>; T. Y. Kositskaya<sup>1</sup>; K. A. Muravin<sup>1</sup>; L. V. Chugaev<sup>1</sup>; <sup>1</sup>Norilsk Nickel RJS, Gipronickel Institute JS, Saint-Petersburg Russia

At Gipronickel Institute the technological flowsheet of pressure leaching of copper from rich copper concentrates (i.e. containing: Cu -59-75%; Ni -0.5-4.64%; Fe -0.2-1.3%; S -21.8-26.9%) was developed. As a result, the possibility of deep decomposition of copper-containing minerals with extraction of elemental sulphur (up to 90-95%) was established. The obtained sulphur concentrates contain 80-90% of elemental sulphur, which can be separated from sulphide residue through autoclave melting and settling. As a rule, sulphide concentrates remaining after extraction of sulphur contain up to 1-2% of noble metals. The sulphide concentrate can be purified to the level of rich concentrates or pure metals using the well-known methods as in the case of tankhouse slimes. The presented research specifies the parameters of main operations: pressure leaching and sulphur extraction. It was established that 98% of copper could be transferred into solution at temperatures of 108-110°C and oxygen partial pressure 0.4-0.6 MPa. The above process may be realised as a one- or two-stage operation. Applying the two-stage operation will reduce the total residence time of the material in an autoclave and thus, the total number of required autoclaves. Experiments were carried out in autoclaves of various volumes using the products of nickel matte processing.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Recycling, Waste Treatment and Environmental Issues II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM                      Room: Leucadia  
March 4, 2003                    Location: San Diego Marriott Hotel

*Session Chairs:* Jesús Contreras, Atlantic Copper S.A., Huelva Spain; Florian Kongoli, FLOGEN Technologies Inc., Matls. Tech. Dept., Montreal, Quebec H3S 2C3 Canada

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### 8:30 AM Keynote

**Metal Recycling and Waste Treatment:** *Yoshihiko Maeda*<sup>1</sup>; <sup>1</sup>Dowa Mining Company, Ltd., 1-8-2 Marunouchi, Chiyoda-Ku, Tokyo 100-8282 Japan

It is said that the 21st century will be an era to remedy global environment. To reserve natural resources for the future and to avoid dispersion of heavy metals, after usage, not to cause pollution problem, it is extremely important to recycle heavy metals as much as possible by reasonable recovery procedures. Nonferrous metal industry is expected to play a great role in recycling of heavy metals that are originally their products. From the depressed metal price experience in 1980th in Japan due to the sudden change in current exchange rate between US dollar and Japanese yen, one of major nonferrous metal company, Dowa Mining, has diversified its business area not only to so-called down stream, but also to environmental business including metal recycling, industrial waste treatment and soil remediation by utilizing technology and facilities once used or still used for mining and smelting of copper, zinc, lead and precious metals. In this paper, some of these applications will be presented.

### 9:05 AM

**The Decomposition Mechanism of Precursor 2,4,5-Trichlorophenol for 2,3,7,8-TCDD Using Ab Initio Molecular Orbital Method Calculation:** *Takashi Araki*<sup>1</sup>; *Mitsuhiro Hirota*<sup>1</sup>; *Akio Fuwa*<sup>1</sup>; <sup>1</sup>Waseda University, Grad. Sch. of Sci. & Eng., Oookubo 3-4-1 Soudai-rikou 60-110, Sinjuku-ku, Tokyo 169-8555 Japan

Dioxins (a generic term for PCDDs and PCDFs) have been the most serious air pollutants, because these compounds have highly acute and chronic toxicity. At present, removal and inhibition techniques of dioxins emission have been proposed by several workers, and catalytic decomposition method has been believed to be one of the most useful methods. However, the reaction mechanism on this method has not yet been clarified. In this work, we have paid attention to behavior of 2,4,5-trichlorophenol, since this is the most generative precursor of 2,3,7,8-TCDD of the highest toxicity among PCDDs congeners. Such a study that clarifies the decomposition reaction mechanism of 2,4,5-trichlorophenol may give us important knowledge for advancing the dioxin emission control. Thus, we have studied the decomposition mechanism of 2,4,5-trichlorophenol using ab initio molecular orbital method calculation.

### 9:30 AM

**Scrap Combination for Recycling Valuable Metals: Direct Extraction and Recovery of Neodymium Metal from Magnet Scraps:** *Toru H. Okabe*<sup>1</sup>; *Osamu Takeda*<sup>2</sup>; *Kazuhiro Fukuda*<sup>3</sup>; *Yoshiaki Umetsu*<sup>4</sup>; <sup>1</sup>The University of Tokyo, Inst. of Industl. Sci., 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan; <sup>2</sup>Santoku Company, Ltd., 4-14-34, Fukae-Kitamachi, Higashi-nada-ku, Kobe 658-0013 Japan; <sup>3</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls. (IMRAM), 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

A fundamental study was conducted with the purpose of establishing an environmentally sound recovery process for recycling valuable

metals by combining scraps containing valuable metals. As an example, we investigated direct extraction and recovery of neodymium (Nd) in magnet scraps by utilizing liquid metal as an extraction agent. It was found that liquid magnesium (Mg) or silver (Ag) are suitable extraction agents, and can extract Nd out of iron alloys with high efficiency at around 1100 K. The newly developed extraction apparatus for Nd is a mechanically simple, static device without moving parts, where the Mg extraction medium circulates due to temperature difference inside the reaction vessel. This developed device can simultaneously accomplish continuous extraction of metal Nd from scraps, re-extraction of Mg from Mg-Nd alloy, and eventual recovery of pure Mg. As a result, metal Nd with 98% purity was directly recovered from magnet scraps under certain conditions. It was also shown that the extraction agent Mg could be reused. The results of this investigation show the possibility of establishing a procedure for directly extracting metal Nd in pure metal form without oxidization.

### 9:55 AM

**Distribution Behaviors in Recycling of Copper from the Waste:** *Junzo Hino*<sup>1</sup>; <sup>1</sup>Toho Titanium Company, Ltd., Titanium Div., 3-3-5 Chigasaki, Chigasaki, Kanagawa-Pref. 253-8510 Japan

Most of the waste that contains a small portion of copper is landfilled. The recycling process of copper from the waste, such as shredder residue, should be developed in order to save mineral resources and prevent environmental pollution. Shredder residue generated from disposed automobiles and electric appliances consists of many types of plastics, glasses and metals. The combustion heat of plastics is efficiently used for melting in the recycling process, which consists of melting and reduction. The knowledge of distribution behaviors of main components is available to develop the process, because the waste contains a lot of different kind of components. Distribution behaviors in the recycling process are evaluated by using the thermodynamic calculation program, HSC Chemistry. The calculation results are compared with the practical operation data of the recycling process and discussed.

### 10:20 AM Break

### 10:35 AM Invited

**Environmental Policy and Continuous Improvement in Atlantic Copper:** *Jesús Contreras*<sup>1</sup>; *Adelino Alonso*<sup>1</sup>; *Pedro Hidalgo*<sup>1</sup>; *Miguel Palacios*<sup>1</sup>; <sup>1</sup>Atlantic Copper S.A., Huelva 21001 Spain

Since the commencement of its activities in Huelva in 1970, Atlantic Copper has maintained a course of action that has been more demanding than the successive environmental legislations current at different times. As its primary objective it has sought compatibility between the protection of the environment and both its industrial activity and the social and economic development of the area in which its Metallurgical Complex is located. For this reason, since the seventies it has maintained a continuous programme of investments which have allowed it to attain its present environmental situation. As a consequence of the Environmental Policy of Atlantic Copper, in April 1998 it obtained certification for its Integrated System of Environmental Management (SIGMA) according to international standard ISO-14001, and under European Community Regulation 1836/93 for the Eco-Management and Eco-Audit System (EMAS). The SIGMA formalises the environmental management practices of Atlantic Copper and engages it to have available a system that can be fully audited. Atlantic Copper was the first European company in the non-ferrous metallurgical sector to obtain both the UNE-EN-ISO 14001 certification and the EMAS registration. The present paper reviews the actions by Atlantic Copper in environmental matters that have allowed it to achieve its present position. It also describes the coming stages of improvement planned and the modifications to be carried out in the near future, in particular the criteria for the selection of technologies on the basis of the concept of BAT (Best Available Techniques) introduced by the European Union, and always guided by the final objective of converting Atlantic Copper into a reference within the sector, comparable to the best designed and operated installations in the world.

### 11:05 AM Invited

**Phytoremediation Potential of Several Plants for Nickel Contaminated Soils:** *A. Cullaj*<sup>1</sup>; *A. Hasko*<sup>2</sup>; *Florian Kongoli*<sup>3</sup>; <sup>1</sup>University of Tirana, Dept. of Chem., Tirana Albania; <sup>2</sup>Agricultural University of Tirana, Dept. of Agronomy, Tirana Albania; <sup>3</sup>FLOGEN Technologies, Inc., 5757 Decelles Ave., Ste. 511, Montreal, Quebec H3S 2C3 Canada

Several industrial sites suffer from the contamination of soils from heavy metals, which are emitted among others by anthropogenic mining and metallurgical activities. Effective and economic physicochemical technologies for remediation of these sites remain elusive and costly. A new alternative remediation technique is the so-called phytoremediation. This is based on the ability of some plants to accu-

multate very high concentrations of metals from soils and thus providing the basis for a remediation of the contaminated sites. This technique, is an emerging branch of natural biotechnology and has several advantages compared to the sophisticated physicochemical techniques of soil remediation. It is not only environmentally friendly and pleasing to the eye but also its costs are quite low since it is solar driven, and, in some cases, plants can accumulate metals to such levels that economic mineral recovery maybe feasible even in conventional Ni refinery or smelting operations. In this work, the potential of many plants to accumulate nickel has been investigated in order to identify the species which offer the best phytoremedial potential for nickel contaminated soils. Field surveys have been made in five nickel-containing sites in order to identify the nickel tolerant species that have spontaneously grown in contaminated soils. Atomic Absorption Spectrometry measurements were carried out on 145 different plants collected. 16 of them were identified as having an hyper ability to accumulate nickel since they contained more than 10 000 mg Ni per kg (DW). Seven taxa are of *Alyssum* genus and one of *Bornmuellera* genus of Cruciferae. The highest accumulation of nickel was present in aerial parts of *Alyssum murale* var. *chlorocarpum* Hauskn (25 500 mg/kg) and *Alyssum markgrafii* O.E. Schulz (23 700 mg/kg). The seeds germinated are more evidenced at *A.m.var. chlorocarpum*, about 63%. These plants are suggested as the most promising species to be used for phytoremediation purposes in nickel contaminated soils.

**11:35 AM**

**Development of Roasting Process for Fly Ash from Municipal Incinerators:** *Mototsugu Matsuno*<sup>1</sup>; *Katsuhiko Tomoda*<sup>1</sup>; *Junnichi Takahashi*<sup>1</sup>; <sup>1</sup>Sumitomo Metal Mining Company, Ltd., Energy & Environ. Business Div., 5-11-3 Shinbashi Minato, Tokyo 105-8716 Japan

Several types of process have been developed for treating fly ash generated from municipal incinerators. The incinerator fly ash contains not only toxic metals such as lead and cadmium, but also dioxins. A new process was examined in the present study. Fly ash is formed into green pellets with some additives, and the pellets are then roasted to eliminate or stabilize the toxic metals, and to decompose dioxins. The roasted pellets become harmless through this process, and are recycled as artificial lightweight aggregates. Volatilized metals are collected as secondary fly ash, and recovered at non-ferrous smelting plants. A new pilot plant of this process, with a capacity of approximately 100 kg/hr, was installed and several types of test were carried out. The characteristics of this process technology are complete reduction of heavy metals, strict stabilization of residual metals and high-strengthen pellets production by sintering. Mechanism of roasting is also analysed.

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## **Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Lead-Zinc**

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM                      Room: Santa Rosa  
March 4, 2003                    Location: San Diego Marriott Hotel

*Session Chairs:* Yong Hack Lee, Korea Zinc Company Ltd., Seoul Korea; Andreas Siegmund, RSR Technologies Inc., Dallas, TX 75207 USA

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**8:30 AM Keynote**

**Modern Applied Technologies for Primary Lead Smelting at the Beginning of the 21th Century:** *Andreas Siegmund*<sup>1</sup>; <sup>1</sup>RSR Technologies, Inc., 2777 Stemmons Freeway, Ste. 1800, Dallas, TX 75207 USA

During the decade of the nineties the conventional method of primary lead smelting (sinter machine/blast furnace) was successfully challenged by the introduction of novel direct and continuous smelting processes. These modern technological innovations like the QSL, Kivcet, and Isa/Ausmelt process, became more than major competitors and in combination with a significant shift in market structure as well as more stringent government regulations, caused radical changes in many different aspects. They have proven to be economically and environmentally viable. The intensification of the metallurgical reaction by applying the bath or flash smelting principle in conjunction with the usage of oxygen resulted in cost savings and a higher flexibility with respect to raw materials and additives usage. By synchronizing individual auxiliary plant sections with the smelting process nearly optimum energy exploitation, a virtually waste-free production and low-emission mode of operation is achieved. The primary lead industry is at a crossroad where novel high-energy efficient technologies will gradually substitute the sinter-blast furnace operation in the new millennium.

**9:05 AM**

**Thermodynamic Study on Recovery of Lead and Antimony from a Used Lead-Battery:** *Satoshi Itoh*<sup>1</sup>; *Atsushi Kikuchi*<sup>1</sup>; *Mitsuhsisa Hino*<sup>2</sup>; <sup>1</sup>Tohoku University, Grad. Sch. of Eng., Dept. of Metall., Aramaki-Aza-Aoba 02, Aoba-ku, Sendai 980-8579 Japan; <sup>2</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., Katahira, Aoba-ku, Sendai 980-8577 Japan

Phase equilibria and activities of the components in the liquid lead-antimony-oxygen ternary system, which is of fundamental importance for discussing the recovery of lead and antimony from a used lead-battery, have been investigated at 1173 and 1223 K. The two liquid phases of metal and oxide were observed at the temperatures studied, and the tie lines indicating isoactivities were determined. The activities of PbO, SbO<sub>1.5</sub> and Sb<sub>2</sub>O<sub>3</sub> in the PbO-SbO<sub>1.5</sub> and PbO-Sb<sub>2</sub>O<sub>3</sub> pseudo-binary systems were then obtained by applying the Gibbs-Duhem equation to the phase relation of metal-oxide equilibrium. Both in the pseudo-binary systems the activities exhibit negative deviations from Raoult's law. The vapor pressures of lead, antimony and lead oxide, antimony oxide were calculated by using the activities of the components in the lead-antimony-oxygen ternary system. As a result, an oxidation of antimony concentrated in an anode slime followed by evaporation as antimony oxide Sb<sub>4</sub>O<sub>6</sub> was found to be considerably effective for the recovery of lead and antimony from a used lead-battery.

**9:30 AM Invited**

**Simulation of Imperial Smelting Furnace Operation Using a Mathematical Model:** *Kenji Matsuzaki*<sup>1</sup>; *Fumio Tanno*<sup>2</sup>; *Akio Fuwa*<sup>3</sup>; <sup>1</sup>Mitsui Mining & Smelting Company, Ltd., Corporate R&D Ctr., 1333-2 Haraichi, Ageo-shi, Saitama 362-0021 Japan; <sup>2</sup>Metal Economics Research Institute, Japan, 2-6-4 Toranomon, Minato-ku, Tokyo 105-0001 Japan; <sup>3</sup>Waseda University, Dept. of Matls. Sci. & Eng., 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555 Japan

A mathematical simulation model of the Imperial Smelting Furnace Operation has been developed to clarify the internal state of the furnace and to improve the furnace operation. The model consists of top, shaft and bottom regions. Analysis in the shaft region is based on differential heat and materials balances taking account of reaction kinetics and heat transfer rate, and those in the top and the bottom regions are based on heat and mass balances under steady state condition. Longitudinal distributions of process variables such as temperatures of gas, sinter and coke, gas composition and reaction extend under a practical operating condition are then calculated. The ISF performance under various operating conditions has also been estimated. A new process for zinc smelting has also been proposed and analyzed using this model.

**10:00 AM**

**The Nature of Accretion Formation During Roasting of Zinc Concentrates in Fluidized Bed Furnace:** *N. M. Komkov*<sup>1</sup>; *V. A. Luganov*<sup>2</sup>; <sup>1</sup>D. Serikbaev East-Kazakhstan Technical University, 19 Serikbayev Str., Ust-Kamenogorsk 492010 Kazakhstan; <sup>2</sup>K. Satpaev Kazakh National Technical University, 22 Satpaev Str., Almaty 480013 Kazakhstan

The main operation of obtaining zinc from sulfide raw materials by hydrometallurgical technology is oxidizing roasting of zinc concentrates in fluidized bed furnaces. The technical-economic parameters are determined by the parameters of the roasting process which in their term depend on the composition of initial raw materials, the temperature of the bed and on other factors. Keeping up of the predetermined temperature of roasting is due to the change of specific efficiency as well as to quantity of heat removed from the bed. The efficiency the caissons depends in a high degree on the composition and thickness of the accretion formed on the surface of the caissons.

Forecasting the roasting results is impossible unless we know the accretion formation mechanism. The aim of the present paper is the thermodynamic analyses of behavior of the charge compositions under roasting and determination of the potential mechanism accretion formation. The thermodynamic analyses show that under conditions of oxidizing roasting the thermodynamic probability of zinc sulfate formation is higher than the probability of oxide formation till temperature of 873 K is reached. The thermodynamic probability of lead sulfate formation is higher than the probability of oxide formation in the whole temperature range of roasting. The probability of formation of ferrites and silicates of zinc only insignificantly decreases the sulfate stability. The results of investigation of accretion composition formed under roasting of concentrates with the particle size less than 0.02 mm (60%), containing 65% of sphalerite (ZnS), 12% of pyrite and chalcopyrite (FeS<sub>2</sub> and CuFeS<sub>2</sub>) each, 3% of galenite (PbS), 7% of silica and other non-ore minerals, have shown the following. The composition of accretion varies depending on the depth of the accretion layer. The accretions on the caissons and the thermo-siphons consist mostly of zinc sulfate (more than 50%). The accretions of forchamber consist mostly of zinc oxide. They also contain ferrites and silicates. Formation of sulfate zinc accretion on cold parts of fluidized bed furnace (on the caissons and on the thermo-siphons) may be explained by a lower temperature on the surface and probably by catalytic influence of oxides present at caissons and thermo-siphons surface on the formation of SO<sub>2</sub> and sulfates. The nature of the accretion structure on the hotter parts of the furnace may supposedly be explained by formation of elemental vaporous zinc during roasting.

#### 10:25 AM Break

#### 10:35 AM Keynote

**The Experience of Lead Direct Smelting in Korea Zinc's Onsan Refinery:** *Yong Hack Lee*<sup>1</sup>; Young Min Park<sup>1</sup>; <sup>1</sup>Korea Zinc Company, Ltd., 142 Nonhyon-dong Kangnam-Ku, Seoul 135-749 Korea

Nonferrous smelting processes have been rapidly changed since the beginning of 1980. The copper smelting technology has been changed to the Flash Smelting and MIB process from the conventional Blast Furnace process. In the field of lead smelting, the technology has changed from Blast Furnace Smelting to the Direct Smelting such as QSL and KIVCET. At 1992, Onsan Refinery of Korea Zinc successfully commissioned Direct Smelting QSL technology for lead. The QSL can produce more than 160,000 ton per year of lead bullion from lead concentrate and various scraps. Moreover, since 2000, the TSL (Top Submerged Lance) Technology utilizing the same Direct Smelting process has been successfully commissioned to treat low grade of lead concentrate as well as lead sulfate residue produced from a hydrometallurgical zinc plant. This paper presents and compares the energy flows of lead smelting processes such as a conventional process and the Direct Smelting Processes plotted on the Pb-O-S phase diagram. The differences of enthalpy and free energy change are also discussed based on the each smelting path. The potential diagram of CO/CO<sub>2</sub> suggests how to control the oxygen potential in furnace. Also, it describes the recent operational experience in TSL plant of Onsan Refinery with necessary mass balance of key elements.

#### 11:10 AM Invited

**Direct Production of Metallic Zinc from EAF Dust:** *Takeshi Azakami*<sup>1</sup>; Hirofumi Sugimoto<sup>2</sup>; Sachio Kojima<sup>2</sup>; <sup>1</sup>Saitama Institute of Technology, Grad. Sch. of Eng., Okabe, Saitama 369-0293 Japan; <sup>2</sup>Sotetsu Metal Company, Ltd., Bandai 1414, Bandai, Fukushima 969-3301 Japan

In Japan, more than 500 thousand tons of EAF dust is generated every year. Zinc source in the dust reaches 17 to 25% of annual zinc production in Japan. Most of this zinc in EAF dust has been recovered as crude zinc oxide by carbon reduction in rotary kilns or other furnaces. Produced crude zinc oxide is valued very cheap because it has to be treated again as a raw material of zinc pyrometallurgy. With the view of direct production of metallic zinc, fundamental experiments were carried out by applying "Iron Reduction Vaporization Method". The purpose of the study is to cut down the treatment costs and to make more profit on dust treatment process. Also, by this process, decreasing in CO<sub>2</sub> generation would be attainable. By larger scale tests, zinc ingots have been produced, and industrialization of the process will be hopefully expected.

#### 11:40 AM

**Installation of Arsenic Removal into the Hematite Process:** Hitoshi Msauda<sup>1</sup>; Shigeki Sato<sup>1</sup>; Yoshito Kudo<sup>1</sup>; *Yutaka Shibachi*<sup>1</sup>; <sup>1</sup>Akita Zinc Company, Ltd., Hematite, 217-9 Shimo-Kawabata Furumichi Iijima, Akita 011-0911 Japan

The Iijima Zinc Refinery started operation in 1972, and has an annual capacity of 200,000t-Zn today. The hematite process was employed for the first time and we have been pursuing the ideal of waste-free refinery for 30 years. In recent years, however, only a half of the hematite produced could be sold to the cement industry and reducing arsenic level had been anticipated for selling them all. The arsenic cementation process with zinc powder, which was developed in the long time laboratory works, was determined best for hematite process among some options. The construction works started in 2000 and was put into operation in 2001, and all hematite were sold to the cement industry in the same year. The outline of this project, present operation and technical issue will be reported in this paper.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: General II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C5 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday AM Room: Point Loma  
March 4, 2003 Location: San Diego Marriott Hotel

*Session Chairs:* Ramana G. Reddy, The University of Alabama, Dept. of Metallurgl. & Matls. Eng., Tuscaloosa, AL 35487-0202 USA; Brajendra Mishra, Colorado School of Mines, Metallurgl. & Matls. Eng., Golden, CO 80401 USA

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#### 8:30 AM Keynote

**Application of Molten Salts in Metals Production:** *Brajendra Mishra*<sup>1</sup>; <sup>1</sup>Colorado School of Mines, Metallurgl. & Matls. Eng., 1500 Illinois St., Golden, CO 80401 USA

Molten Salt electrolytic processes offer unique opportunities to extract and refine metals where gaseous or metallothermic reduction, hydrometallurgical extraction and aqueous electrolytic methods are thermodynamically constrained. Production of aluminum and magnesium by molten salt electrolysis are well known commercial processes. Several other reactive metals, such as lanthanides and actinides, as well as beryllium and calcium, make use of molten salt processing for extraction and refining. This presentation describes the science of molten salt chemistry and electrochemistry for winning and refining of several metals. In addition, recovery of metals from waste process salts by molten salt reduction as well as oxidation have been discussed. Material issues in design of molten salt reactors have been included. Various applications have been presented through case studies. Experimental data have been included to justify the suitability as well as limitations of these specific processes.

#### 9:05 AM

**Thermogravimetric Study of the Sulfurization of TiO<sub>2</sub> Using CS<sub>2</sub> and H<sub>2</sub>S:** *Nobuaki Sato*<sup>1</sup>; Jhon Cuya<sup>1</sup>; Katsutoshi Yamamoto<sup>1</sup>; Atsushi Muramatsu<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

Titanium dioxide is the well-known catalyst for the photodecomposition of water in uv region. On the other hand, titanium sulfides absorb the visible light, though it is rather unstable in water because of its photo-dissolution. In this regard, partially sulfurized TiO<sub>2</sub> is expected to be chemically stable and have an enhanced photocatalytic activity compared with TiO<sub>2</sub>. For the analysis of sulfurization behavior of TiO<sub>2</sub>, thermogravimetric study on the sulfurization of TiO<sub>2</sub> was made using a thermo-balance with a quartz spring. In the case of CS<sub>2</sub>, sulfurization reaction started at around 773 K with heating rate of 1 K/min. The weight increase curve showed a maximum of c.a. 30 wt% at around 1023 K and then gradually decreased to c.a.12 wt% at 1273 K. This would be caused by the formation of TiS<sub>2</sub> followed by the

decomposition of TiS<sub>2</sub> to lower sulfides. The sulfurization behavior of TiO<sub>2</sub> using H<sub>2</sub>S was also investigated compared with that of CS<sub>2</sub>.

**9:30 AM**

**Decomposition of Sulfide Concentrates Under Concentrated Solar Radiation—A Novel Approach to Effect the Direct Decomposition of Sulfides:** Lenny Winkel<sup>1</sup>; Christine Guesdon<sup>1</sup>; Marcel Sturzenegger<sup>1</sup>; <sup>1</sup>Paul Scherrer Institut, High-Temp. Solartech., OVGA/103A, Villigen PSI 5232 Switzerland

The decreasing demand for sulfuric acid as well as attempts to reduce CO<sub>2</sub> emissions stimulated research activities aiming at new process routes for metal extraction. The most intriguing approach to avoid formation of sulfur dioxide (SO<sub>2</sub>) and that of intermediate oxides is the direct conversion of metal sulfides into the metal and elemental sulfur. A promising path to realize the direct conversion is the use of concentrated solar radiation. Thermodynamic calculations suggest that many non-ferrous metal sulfides decompose into the metal and sulfur at temperatures between 1300 and 2000°C. Such temperatures are readily accessible in solar chemical reactors and metal extraction with high maximum efficiencies and reduced or zero emission of SO<sub>2</sub> and CO<sub>2</sub> can be envisioned. Experimental work on solar metal extraction has been initiated for zinc and copper. Chemical reactivity studies by means of thermogravimetry and powder x-ray diffractometry have shown that extraction of copper is easier to effect than that of zinc: During the decomposition of copper sulfides gaseous sulfur naturally separates from liquid copper, while decomposition of zinc sulfide generates a vapor with zinc and sulfur being mixed. To prevent zinc and sulfur from reacting back to the parent zinc sulfide, additional measures, e.g. fast cooling, are required. Chemical equilibrium calculations have confirmed that the solar decomposition of copper sulfide concentrates provides an additional benefit with regard to removal of volatile impurities. Since the solar decomposition can be conducted in absence of oxygen, slag forming reactions will be suppressed and impurities such as arsenic or antimony can easily be separated from copper metal by evaporation. After a short description of the novel approach the paper will firstly report on the chemical equilibrium calculations carried out for evaluating the potential of impurity removal and secondly present an imaging furnace, set up for studying the decomposition of sulfides at temperatures up to 2000°C.

**9:55 AM**

**Removal of Boron from Metallurgical-Grade Silicon by Applying CaO-Based Flux Treatment:** Mitsuru Tanahashi<sup>1</sup>; Hideo Nakahigashi<sup>1</sup>; Kunihiko Takeda<sup>1</sup>; Chikabumi Yamauchi<sup>2</sup>; <sup>1</sup>Nagoya University, Dept. of Matls. Sci. & Eng., Grad. Sch. of Eng., Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan; <sup>2</sup>Chubu University, Dept. of Mech. Eng., Sch. of Eng., 1200 Matsumoto-cho, Kasugai, Aichi 487-8501 Japan

In order to develop economical production process from metallurgical-grade silicon (MG-Si) to solar-grade (SOG-Si), removal behavior of boron from molten MG-Si was investigated at 1773 K by two following CaO-based flux treatment processes, which can establish special condition of both high basicity of flux and high oxygen partial pressure at boron removal reaction sites: [1] Boron removal from MG-Si by flux addition onto the molten silicon followed by oxygen gas injection into the melt (Two-stage connecting process). [2] Boron removal from MG-Si by simultaneous injection of flux powders and oxygen gas into the molten silicon (Simultaneous injection process). By these treatment processes, especially simultaneous injection process using a flux powder injection equipment, boron content in MG-Si can be reduced efficiently. Based on the results obtained, optimum conditions for boron removal by the flux treatment were examined from the viewpoints of operating time, oxygen gas flow rate, and so on.

**10:20 AM Break**

**10:40 AM**

**Sulfur and Oxygen Potential Ratios Prediction in Copper Flash Smelting Plants Using Reddy-Blander Model:** Bora Derin<sup>1</sup>; Ramana G. Reddy<sup>1</sup>; <sup>1</sup>Istanbul Technical University, Dept. of Metallurg. & Matls. Eng., Istanbul 80626 Turkey; <sup>1</sup>The University of Alabama, Dept. of Metallurg. & Matls. Eng., Tuscaloosa, AL 35487-0202 USA

In smelting furnace conditions, copper losses in liquid fayalitic slags are both as entrained matte and as chemically dissolved species. Using Reddy-Blander (RB) model, the entrained sulfur content in the slags and the exact potential ratios of sulfur and oxygen for several copper flash smelting plants were derived. The sulfide capacities (Cs) of six different flash smelting plants multicomponent (FeO-Cu<sub>0.5</sub>-CaO-MgO-FeO<sub>1.5</sub>-AlO<sub>1.5</sub>-SiO<sub>2</sub>) slags were calculated. The log (PO<sub>2</sub>/PS<sub>2</sub>) versus matte grades of the industrial furnaces was determined. The PO<sub>2</sub>/PS<sub>2</sub> ratio increases with an increase of copper grade and for the

copper flash smelting condition, the calculated PO<sub>2</sub>/PS<sub>2</sub> ratios were found to be in very good agreement with the experimental and plant data. Hence, the RB Model predicted that sulfide capacity could be calculated a priori, based on a simple solution model and on knowledge of the chemical and solution properties of sulfides and oxides.

**11:05 AM Invited**

**Roasting Mechanisms of Impure Zinc Concentrates in Fluidised Bed:** Maija-Leena Metsäranta<sup>1</sup>; Pekka A. Taskinen<sup>1</sup>; Satu K. Jyrkönen<sup>1</sup>; Aija Rytioja<sup>2</sup>; Jens Nyberg<sup>2</sup>; <sup>1</sup>Outokumpu Research, PO Box 60, Pori 28101 Finland; <sup>2</sup>Outokumpu Zinc, PO Box 26, Kokkola FIN-67101 Finland

The behaviour of copper and lead in zinc roasting has been studied in laboratory scale roasting and large scale trials in an industrial fluidised bed, with the background of Outokumpu Kokkola Zinc smelter. Commercial zinc concentrates with a low and high ( up to 3 wt % ) copper content and with a low and high ( up to 3.5 wt % ) lead content were oxidized to various desulphurisation degrees in the fluidised bed to establish the reaction mechanisms and the paths for copper and lead oxidation in the roasting. Influences of the agglomerate size on the roasting kinetics and micro-scale phenomena were also determined. Optical microscopy was used on the calcine and the findings are presented as numerous photographs of the polished cross sections. SEM/EDS techniques were used for analyzing chemically the phases and particle morphologies present in the samples. Computational thermodynamics was applied to the complex phase equilibria occurring during roasting in the agglomerating calcine. A complete oxidation of zinc concentrate with a high copper and lead content requires a careful control of oxygen coefficient in the roasting in order to maintain a stable operation of the fluidised bed. Oxygen coefficient thus seems to have a significant impact on the hydrodynamic stability of the fluidised bed with fine raw materials.

**11:30 AM Invited**

**Some Aspects of Cleaning of Ni, Co and Cu-Containing Slags Via Oxide Melt Blowing by Reducing Gases:** L. Sh. Tsemekhman<sup>1</sup>; A. G. Ryabko<sup>1</sup>; L. B. Tsybulov<sup>1</sup>; M. V. Knyazev<sup>1</sup>; V. B. Fomichev<sup>1</sup>; A. A. Ryumin<sup>1</sup>; L. A. Pavlina<sup>1</sup>; <sup>1</sup>AO "Gipronickel", 1 Gromzdansky Pr., Saint-Petersburg 195220 Russia

One of the methods of cleaning slags containing Ni, Co, and Cu is their blowing by reducing gas mixtures formed in the process of gas or liquid fuel firing. The investigations carried out by us have shown that the acceptable residual Ni and Co content is achieved by means of natural gas combustion at a <0,7 and solid reducer consumption at the level of 6-10%. The values of cleaning are independent of gas-solid fuel consumption ratio and determined by partial oxygen pressure achieved during both fuels oxidizing. The results obtained from cleaning of industrial slags of different compositions by gas mixtures corresponding by composition to various conditions of natural gas combustion are given in the report. The influence of introduced sulphur-containing collector on the cleaning values, as well as the importance of interaction of produced alloys, mattes, slags, and a gas phase are considered.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Slags and Fluxes

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday PM

March 4, 2003

Room: Solana

Location: San Diego Marriott Hotel

*Session Chairs:* Kazuki Morita, The University of Tokyo, Dept. Metall., Tokyo 113-8656 Japan; Florian Kongoli, FLOGEN Technologies Inc., Matls. Tech. Dept., Montreal, Quebec H3S 2C3 Canada

### 2:30 PM Keynote

**Slags and Fluxes in Pyrometallurgical Processes:** *Florian Kongoli*<sup>1</sup>; <sup>1</sup>FLOGEN Technologies, Inc., Matls. Tech. Dept., 5757 Decelles Ave., Ste. 511, Montreal, Quebec H3S 2C3 Canada

Slags and fluxes are important interexchanged dimensions of pyrometallurgical processes. They can increase the efficiency of the smelting, converting and refining processes and improve the quality of the final products. A good slag, in one hand, should have appropriate physicochemical properties such as low liquidus temperature, optimal viscosity, maximum ability to attract undesirable elements, minimum potential of attracting valuable elements, etc. A good flux, on the other hand, when properly used, can considerably improve the physicochemical properties of the slag since by modifying its chemical composition it can decrease the liquidus temperature, improve viscosity etc. Consequently, the choice of a good slag and the corresponding fluxing strategy has become indispensable in most of industrial processes. However, the properties of multicomponent slags as well as the effect of several fluxes used in practice today are known only empirically. Sometimes they have been globally asserted without taking into account the characteristics of individual processes, the positioning of the initial slag composition or the particularities of certain laboratory procedures used to assert these effects. In the today's reality of frequent changes in the composition of the raw materials and that of the fluxes themselves, in the existing or new developing technologies, the quantification of the physicochemical properties of the multicomponent slags and the effect of fluxes becomes indispensable. This paper reviews the work carried out from the author's group during the last 15 years on the quantification of the physicochemical properties of multicomponent slags and on the effect of fluxes in several smelting and converting processes in close relation to individual characteristics of these processes. Several examples have also been given in order to demonstrate the fact that when taken outside the context some fluxes can become in fact anti-fluxes.

### 3:05 PM

**Phase Diagram of CaO-FeOx-Cu2O Slag Under Copper Saturation:** *Yoichi Takeda*<sup>1</sup>; <sup>1</sup>Iwate University, Fac. of Eng., Ueda 4-3-5, Morioka 020-8551 Japan

The CaO-FeOx-Cu2O slag system has been practically applied to continuous converting of copper, and also has potential for refining of copper. Liquidus lines of the slag system under copper saturation and phase stability diagram for the existing compounds are presented. Slag and copper metal were melted in a magnesia crucible. Liquidus composition was determined by chemical analysis of slag sample saturated solid phase. The temperatures of invariant equilibria were investigated by thermal analyses. Oxygen potentials on the liquidus lines, the univariant and invariant equilibria were extrapolated from the relation between slag composition and oxygen potential, that relation was confirmed in separate experimental work.

### 3:30 PM Invited

**Some Aspects of Calcium Ferrite Slags:** *Sharif Jahanshahi*<sup>1</sup>; <sup>1</sup>CSIRO Minerals, Clayton, Saint-Petersburg, Victoria 3168 Australia

Calcium ferrite slags are often associated with Professor Yazawa due to his pioneering work on thermodynamics of this type of melts. Over the past years CSIRO has invested some effort in studying physicochemical properties of such melts to fill in some of the gaps in our knowledge and explore opportunities for application of the understanding developed. These investigations cover thermodynamics, transport properties of calcium ferrite based slags as well as the kinetics of reactions of such slags with gases or refractories. The present paper provides an overview of some of these studies and highlights some of the interesting behavior of such melts.

### 4:00 PM

**A Counter-Flow Batch Process for Refining Copper Using Sodium Carbonate Slags:** *Hiroshi Hashimoto*<sup>1</sup>; <sup>1</sup>Mitsuru Tanahashi<sup>1</sup>; <sup>1</sup>Hong Yong Sohn<sup>2</sup>; <sup>2</sup>Chikabumi Yamauchi<sup>3</sup>; <sup>3</sup>Kunihiko Takeda<sup>1</sup>; <sup>1</sup>Nagoya University, Dept. of Matls. Sci. & Eng., Grad. Sch. of Eng., Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan; <sup>2</sup>University of Utah, Dept. of Metallurg. Eng., 135 S. 1460 E., Rm. 412, Salt Lake City, UT 84112-0114 USA; <sup>3</sup>Chubu University, Dept. of Mechl. Eng., Sch. of Eng., 1200 Matsumoto-cho, Kasugai, Aichi 487-8501 Japan

For the application of sodium carbonate slag treatment to product high purity copper on an industrial scale, the counter-flow batch operation, which can reduce the amount of utilized slag, was proposed from a viewpoint of a post-treatment of slag. Based on the distribution ratios of several impurities between the slag and molten copper determined previously, the effectiveness of this operation is discussed using a mathematical model and confirmed experimentally. According to the model, the slag consumption to remove Sb to a required level in case of the counter-flow batch operation is calculated to be around

30% of that in case of an ordinary batch operation, where pure sodium carbonate is used as a slag at every stage.

### 4:25 PM Break

### 4:35 PM Invited

**Dissolution Mechanism and Solubility of Chlorine in the Oxide Melts:** *Kazuki Morita*<sup>1</sup>; <sup>1</sup>Taro Hirosumi<sup>1</sup>; <sup>1</sup>Makoto Miwa<sup>1</sup>; <sup>1</sup>The University of Tokyo, Dept. Metall., 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 Japan

Ecological problems have recently been treated in iron- and steel-making processes, as is seen in the development of waste plastic injection into a blast furnace in Japan. However, we have to develop more effective and more extensive utilization of such a high temperature mass production system for the waste management. At present, waste plastic containing chlorine such as polyvinyl chloride (PVC) cannot be treated due to the problem of dioxine and HCl generation as well as the erosion of refractories. In order to develop the waste treatment system for the materials containing chlorine, its behavior in high temperature furnaces must be predicted and the evaluation of chlorine gas absorption into slags becomes essential, which is also very important for the practical incineration process. However, no data are available regarding the thermodynamic properties of chlorine in molten slags, because it has not been treated as impurities in molten iron such as S, P and N. In the present study, thermodynamic properties of chlorine in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O, CaO-SiO<sub>2</sub>-FeO and CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO slags have been investigated in the present study. The experiments were carried out using gas-slag equilibrium, controlling both PO<sub>2</sub> and PCl<sub>2</sub> simultaneously (PO<sub>2</sub>=10<sup>-6</sup>-10<sup>-19</sup> atm, PCl<sub>2</sub>=10<sup>-6</sup>-10<sup>-13</sup> atm at 1673-1748K), and the solubility of chlorine in the 40mass%CaO-40mass%SiO<sub>2</sub>-20mass%Al<sub>2</sub>O<sub>3</sub> slag was found to vary in proportion to PO<sub>2</sub><sup>1/4</sup> and PCl<sub>2</sub><sup>1/2</sup>. Accordingly, the chloride capacity (C<sub>Cl</sub>), which represents the ability of slags to absorb chlorine, has been defined; The C<sub>Cl</sub> values were observed to increase with increasing slag basicity and temperature, and showed a reasonable relationship with that of C<sub>S</sub><sup>2</sup>.

### 5:05 PM Invited

**Selection of Slag Composition and Structure for Autogenous Smelting Process to Produce White Metal Using the Basic Developments of Prof. A. Yazawa:** *V. M. Paretsky*<sup>1</sup>; <sup>1</sup>A. V. Tarasov<sup>1</sup>; <sup>1</sup>State Research Center of Russian Federation, State Rsrch. Inst. of Non-Ferrous Metals "Gintsvetmet", 13 Acad. Korolyov St., Moscow 129515 Russia

The basic work conducted by Prof. A. Yazawa has demonstrated that in order to ensure single-stage white metal production by autogenous smelting of copper sulfide raw materials, it is most favorable to use highly basic slags, in particular oxide systems CaO-FeO-Fe2O3-SiO2. The main advantage of this system is its homogeneity at normal smelting temperatures (1200-1400°C) and within the common ranges of calcium-to-iron ratios under high partial oxygen pressures. Ferrite-calcite slags proposed by Prof. A. Yazawa and his followers found practical use for the first time in the well-known Mitsubishi process. In order to provide a more rigorous substantiation of the selection of the slag composition for the autogenous smelting to produce white metal, special studies have been conducted in the Gintsvetmet Institute to investigate the composition and structure of slags produced on a semi-commercial scale when testing the KFP and FBP processes for white metal smelting, as well as the slag obtained in a full-scale KFP furnace at the Almalyk copper smelter. These studies were conducted using mineralogical microscopy techniques, a Cameca microprobe and nuclear gamma-resonance (NGR) spectroscopy. Studies were carried out using solidified and quenched slags with different cooling rates: 103°C/sec (bar sample) and 10<sup>6</sup>°C/sec (superfast quenching by spinning-disc method). In the latter case, the structure of liquid slag was preserved (super-cooled liquid) permitting more definite assessment of the true structure of slag in molten state. The NGR-spectra obtained have indicated that: · bar sample (quenching rate of 10<sup>3</sup>°C/sec) characterizes an intermediate state between liquid and solidified slag (60% fyalite and 40% vitreous phase); · two types of positions occupied by Fe2+ ions have been identified: tetrahedral (A-positions) and octahedral (B-positions); it should be pointed out that Fe2+ ions occupy preferably positions in octahedral vacancies, while Ca2+ ions occupy only octahedral vacancies and Si4+ ions only tetrahedral vacancies; · with an increase in the Ca2+/Fe2+ ratio the proportion of Fe2+ ions in A-positions increases and that in B-positions decreases resulting in a lower probability of replacement of Fe2+ ions with Cu2+ ions which are located only in B-positions; · an increase in the SiO2 concentration in slag results in occupation of A-positions with Si4+ ions leaving vacant B-positions for Fe2+ ions, and as a consequence, increasing the probability of copper dissolution in slag; · the total proportion of Fe2+ ions in molten slag increases with a higher concentration of CaO in slag. The investigations conducted have demonstrated why production of high-grade matte or white metal is associated with lower loss of

copper in slag in a series: silicate slag/silicate-calcium slag/ferrite-calcium slag.

### 5:35 PM Invited

**Ferrous Calcium Silicate Slags in Direct to Blister Flash Smelting:** *Asmo Vartiainen*<sup>1</sup>; Ilkka V. Kojo<sup>2</sup>; Cesar Acuña Rojas<sup>3</sup>; <sup>1</sup>Outokumpu Research Oy, Pori 28101 Finland; <sup>2</sup>Outokumpu Technology, Espoo 02201 Finland; <sup>3</sup>Codelco, Chuquicamata Chile

Background of Direct-to-Blister Flash Smelting is discussed; especially slag chemistry relating to copper solubility, slag fluidity and impurity behavior. In December, 2000, Mini-pilot Flash Smelting test runs were carried out at Outokumpu Research Oy to produce blister copper from Chilean concentrate and white metal and from a mixture of them. Tested slag types were iron silicate slag, ferrous calcium silicate slag and calcium ferrite slag with different slag compositions and different concentrate/white metal ratios. The test runs were successful. The fluxing effect of copper oxide was clearly demonstrated and ferrous calcium silicate slags remained fluid on a very wide liquidus range. The distribution of arsenic between ferrous calcium silicate slag and blister copper is much higher than between iron silicate slag and blister copper. This successful test run with the new slag type offer new possibilities in Direct-to-Blister process design.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Copper I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday PM                      Room: Santa Rosa  
March 4, 2003                      Location: San Diego Marriott Hotel

*Session Chairs:* Ron M. Sweetin, Mitsubishi Materials Corporation, Oakville, Ontario L6J 4B2 Canada; Mineo Hayashi, PT. Smelting, Gresik E. Java 61151 Indonesia.

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### 2:30 PM Keynote

**Recent Advances in Modern Continuous Converting:** *Motoo Goto*<sup>1</sup>; *Mineo Hayashi*<sup>2</sup>; <sup>1</sup>Port Kembla Copper Pty., Ltd., Military Rd., Port Kembla, NSW 2505 Australia; <sup>2</sup>PT. Smelting, Desa Roomo, Kecamatan Manyar, Gresik, E. Java 61151 Indonesia

Today, Pierce-Smith converters, coupled together with various types of smelting units, are used in most of the world's smelters. However, due to the "batch" processing nature, and problems associated with fugitive emissions during the transfer of melt and blowing stages, this arrangement will unlikely be adopted in future smelters. Modern day alternative processes include the Mitsubishi Process, Outokumpu Flash Smelting and Flash Converting Process, the Noranda Process, and the Ausmelt Process, but only the Mitsubishi Process is a "truly continuous" smelting and converting operation, producing a constant flow of blister without tapping, and is economically proven by long term commercial operations. This paper reviews recent advances in modern continuous converting technologies, with a special section devoted to operation of the "first standalone Mitsubishi C-furnace" coupled together with a Noranda Reactor, at Port Kembla Copper Pty. Ltd. in Australia.

### 3:00 PM

**Development of New Copper Continuous Converter:** *Yasuo Ojima*<sup>1</sup>; *Yasuhiro Kondo*<sup>1</sup>; *Kazunori Kawanaka*<sup>1</sup>; *Keisuke Yamamoto*<sup>1</sup>; *Sumitomo Metal Mining Company, Ltd.*, Niihama Rsrch. Labs., 17-5 Isoura-cho, Otu 145-1 Funaya Saijo, Niihama, Ehime 792-0002 Japan

New copper continuous converting process was investigated to evaluate the possibility to be applied for the commercial operation. The tests were performed with scaling up from the laboratories crucible experiments to the pilot plant test. Bath smelting process with using top submerged lance technology was applied in these tests. Furnace shape was modified to the lengthwise cylindrical shaped one with having the settling area. The furnace monitor was put in the settling area to check inside furnace. FeOx-SiO<sub>2</sub>, FeOx-CaO and FeOx-CaO-SiO<sub>2</sub> based slag system were used for this test to check their efficiency. The optimum slag chemistry to have good metallurgical results in this pilot test was discussed and FeOx-CaO system with adding some SiO<sub>2</sub> was turned out to be preferable, which has not been practically used. In this pilot plant test feeding rate of 1 t/H of solid grain matte was charged consecutively for two weeks and continuous converting could be done successively. This process is supported to overcome the problems of existing processes and be easily applied for existing plants.

### 3:25 PM Invited

**New Approach for the Optimization of Copper Concentrates Flash Combustion by the Control of Blends:** *Roberto Parra*<sup>1</sup>; Roberto Parada<sup>2</sup>; Marcelo Rodríguez<sup>1</sup>; <sup>1</sup>Universidad de Concepción, Dept. of Metallurg. Eng., Edmundo Larenas 270, Concepción Chile; <sup>2</sup>Compañía Minera Disputada de Las Condes, Chagres Smelter, Pedro de Valdivia 291, Santiago Chile

The classic criteria in the preparation of the charge for the smelting of copper concentrates in a flash furnace consider the mass and energy balance from the chemical and mineralogy composition of the concentrates. The operation parameters fixed with this method don't assure the stability of the operation and critical problems of slag quality and dust formation occur very often. This paper present the results of a laboratory test that allows the prediction of the behavior of concentrates blends in view to the minimization of dust formation and magnetite control in the slag. The combustion of different copper concentrates and blends were done in a drop tube furnace. The results show that the magnetite and dust formation don't have a linear behavior with the weight proportion of the blend and some optimal blends of 2 or 3 types of concentrates can be identified. From the reasonable hypothesis that the qualitative behavior of blends in the drop tube represents the real behavior in the burner, the preparation of the charge with this approach could help to solve those operational problems.

### 3:50 PM

**Effect of Magnetic Field on the Rate of Slag Reduction in an Electric Furnace:** *Victor Montenegro*<sup>1</sup>; *Andrzej Warczok*<sup>1</sup>; *Tashiharu Fujisawa*<sup>2</sup>; *Gabriel Riveros*<sup>1</sup>; <sup>1</sup>Universidad de Chile, Av. Tupper 2069, Santiago 2777 Chile; <sup>2</sup>Research Center for Advanced Waste and Emission Management, Furo-Cho, Chikusa-ku, Nagoya 464-8603 Japan

Smelting of copper concentrate in Teniente Converter produces highly oxidized slag, containing from 4 to 10% Cu and from 15 to 25% of Fe<sub>3</sub>O<sub>4</sub>. Copper recovery requires magnetite reduction to a level of 5%, determining the degree of cuprous oxide co-reduction and liberation of copper matte inclusions. Rate of slag reduction is controlled by the mass transfer to the reaction interface. Slag stirring affects the rate of reduction and enhances coalescence of mechanically entrained copper matte inclusions. Slag reduction and sedimentation in AC electric furnace is commonly used method of slag cleaning. Utilization of DC electric furnace creates beneficial conditions introducing slag electrolysis on top of chemical reductions with carbon of coke and electrodes. Application of external magnetic field, interacting with direct current in an electric furnace, induces magnetohydrodynamic phenomena, such as intensive stirring and electromagnetic buoyancy force acting on inclusions. Laboratory scale research in simulated DC electric furnace with superimposed magnetic field, show a significant acceleration of the rate of slag reduction and copper removal. Continuous measurement of gas flow and composition allowed for determination of the reduction rate along the time. Application of external magnetic field in reduction of industrial slag in a crucible simulated DC electric furnace results in the increase of reduction rate from 7 to 15 times, comparing with the identical conditions in AC electric furnace. Interaction of non-homogeneous electric field with crossed permanent magnetic field induces vigorous slag stirring enhancing mass transfer and accelerating the rate of slag reduction. Additional participation of slag electrolysis in magnetite and cuprous oxide reduction as well as acceleration of inclusions settling by electromagnetic buoyancy force affect in slag cleaning intensification.

### 4:15 PM Break

### 4:25 PM Invited

**Ausmelt Technology, Flexible, Low Cost Technology for Copper Production in the 21st Century:** *Joseph Saffra*<sup>1</sup>; *Robert Matuszewicz*<sup>1</sup>;

<sup>1</sup>Ausmelt, Ltd., 12 Kitchen Rd., Dandenong, Melbourne, Victoria 3175 Australia

It has become increasingly evident that sustainable metals production in the 21st century requires producers to balance the needs of cost effective, high value production with that of responsible plant operation. This is becoming more difficult as lower grade and more complex feed materials, including recycled scrap and residues, are being processed to reduce production costs and decrease exposure to primary metal market fluctuations. One particular facet of the metals industry facing these challenges in the 21st century are copper producers. The recent steady decline in the copper price has seen the industry cut expenditure, tighten control on income streams and focus on high returns on capital investment. For these reasons copper producers are looking towards flexible technologies that can deliver high value products, with minimal environmental impact at low capital and low sustainable operating costs. Ausmelt's Top Submerged Lancing (TSL) technology for copper production is a low cost, proven technology for the processing of both primary and secondary copper materials. Both the smelting and converting operations introduce significant advantages in environmental performance, improved process efficiencies and high rates of metal recovery. Ausmelt has made significant gains in the past 4 years in establishing a strong market position for its copper technology. New installations in China, South Africa and India as well as existing operations in Zimbabwe and China have demonstrated its effectiveness. This paper reviews the application of Ausmelt Technology for both smelting and converting of primary and secondary sources. It discusses Ausmelt's design and implementation philosophy, and how this philosophy meshes with the needs of the end user.

#### 4:50 PM

**Quantification of the Liquidus Surface of "Lime Ferrite" Slags at Several Oxygen Potentials:** *Florian Kongoli*<sup>1</sup>; Ian McBow<sup>1</sup>; Akira Yazawa<sup>2</sup>; <sup>1</sup>FLOGEN Technologies, Inc., Matls. Tech. Dept., 5757 Decelles, Ste. 511, Montreal, Quebec H3S 2C3 Canada; <sup>2</sup>Tohoku University, 16-32, Niizaka, Aoba-ku, Sendai 981 Japan

"Lime ferrite" slag with limited silica content has proven to be a valuable choice in the modern processes of copper smelting and converting due to several advantages that this slag offers compared to the classical silicate slags. Nevertheless the liquidus surface of this slag has been experimentally measured only at low oxygen potentials such as in equilibrium with iron or near it and in air. Although most of the smelting and converting processes that use this slag occur at intermediate oxygen potentials, the liquidus surface of this slag is not known at these conditions and the effect of oxygen potential and silica has not been correctly understood. This has brought some confusion in literature as well as in the industrial practice. In this work the liquidus surface of the lime ferrite slags has been quantified by the means of a new thermophysicochemical model and a new type of liquidus surface diagrams which is very convenient for any industrial process that uses lime ferrite slags. These diagrams can be easily used to select the lowest liquidus temperature of lime ferrite slags at a minimum cost and can help design several fluxing strategies in copper smelting and converting processes. The effect of the oxygen potential, silica and copper is also quantified and important industrially related conclusions are drawn.

#### 5:15 PM

**Direct Copper Production by Cyclone Smelting:** *I. Wilkomirsky*<sup>1</sup>; R. Parra<sup>1</sup>; <sup>1</sup>University of Concepción, Dept. of Metallurg. Eng., Edmundo Larenas 270, Concepción 270 Chile

The conventional classical production of blister considers the oxidation of sulfur and iron from copper concentrates in two consecutive steps, although there are no physicochemical reasons why blister copper can not be produced in a single stage. The practical limitations are related to the technology that determines the thermal conditions and the kinetics in different reactors. An analysis was done to determine the conditions required for a cyclonic reactor pilot plant to produce blister copper directly from concentrates. The best metallurgical results were obtained with the cyclonic reactor operating at above 1450°C.

#### 5:40 PM Invited

**The Chilean Copper Metallurgical Industry: An Update:** *A. Valenzuela*<sup>1</sup>; J. Palacios<sup>2</sup>; D. Cordero<sup>3</sup>; M. Sánchez<sup>4</sup>; <sup>1</sup>Chilean Copper Commission, Santiago Chile; <sup>2</sup>University of Atacama, Copiapó Chile; <sup>3</sup>CODELCO, El Teniente Div., Rancagua Chile; <sup>4</sup>University of Concepción, Concepción 270 Chile

In the last years, Chile continue being the top producer of copper, either in the form of concentrates or electrowinning and electrorefining cathodes, the last one obtained from seven smelters, which have carried out several modernization plans either to increase smelting capacity or to achieve environmental regulations established in the Chilean

legislation. This paper updates the current situation of the Chilean copper metallurgical industry developed in the last years, regarding technological innovations in smelters, environmental regulations and presenting solutions for management of SO<sub>2</sub>, particulate matter and arsenic, considering that Chile is the world's largest copper producer. Also, the authors emphasize the important role played by CODELCO Chile, the more important state owner copper company, developing Chilean technologies, as El Teniente Converter and El Teniente Slag Cleaning Furnace.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday PM Room: Pacific  
March 4, 2003 Location: San Diego Marriott Hotel

*Session Chairs:* Adam C. Powell, IV, Massachusetts Institute of Technology, Dept. of Matl. Sci. & Eng., Cambridge, MA 02139-4301 USA; Ryosuke O. Suzuki, Kyoto University, Dept. of Energy Sci. & Tech., Kyoto, 606-8501 Japan

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#### 2:30 PM Invited

**OS Process-Thermochemical Approach to Reduce Titanium Oxide in the Molten CaCl<sub>2</sub>:** *Ryosuke O. Suzuki*<sup>1</sup>; Katsutoshi Ono<sup>1</sup>; <sup>1</sup>Kyoto University, Dept. of Energy Sci. & Tech., Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 Japan

A new cell concept for calciothermic reduction is presented where titanium dioxide is used as the raw material for reduction. It bases on the thermochemical requirement that metallic calcium is needed as the reductant, CaCl<sub>2</sub> as the solvent. The thermodynamic phase equilibria and physical properties are analyzed to optimize the reaction and to separate the product. The reduction system consists in a single cell, where both the reduction reaction and the electrolytic reaction for recovery of reducing agent coexist in the same molten calcium chloride bath. TiO<sub>2</sub> powder is directly top-charged into the molten CaCl<sub>2</sub>. A few %Ca dissolves in the melt, and it constitutes the media with a strong reducing power.  $TiO_2 + 2 Ca + 2 e^- = Ti + 2 Ca^{2+} + 2 O^{2-}$ . Sufficiently deoxidized titanium metal deposits agglomerate rapidly and form granular sponge, which sink down to the bottom of the cell. Both mechanisms of the halide flux deoxidation and the electrochemical deoxidation work efficiently for these fine precipitates. The reducing agent is in situ recovered by electrolysis of CaO, which is supplied as the by-product of reduction. The molten CaCl<sub>2</sub> has a relatively large solubility for CaO. At the anode:  $C + 2 O^{2-} = CO_2 + 4 e^-$ . At the cathode:  $Ca^{2+} + e^- = Ca$ . Some cell designs and modifications are proposed for industrial applications.

#### 3:00 PM

**Preparation of Uniform Ultra-Fine Nickel Oxalate Particles by Chelating Precipitation:** *Huang Kai*<sup>1</sup>; *Chen Hui*<sup>1</sup>; <sup>1</sup>Central South University, Sch. of Metallurg. Sci. & Eng., Lushannanlu, Changsha, Hunan 410083 China

Uniform spherical and fiber-like nickel oxalate particles were prepared by chelating precipitation method, which is by adding the oxalate acid into the solution of ammine nickel chloride. The reactive concentration of the ammine nickel chloride and the oxalate acid are the key factors to the morphologies of the final particles, i.e., low reactive concentrations (<0.1 mol) of the two reagents are in favor of the formation of fiber-like particles while high reactive concentrations are in favor of the formation of spherical particles. The feeding methods and the agitation strength all have effects on the particle forma-

tion, which experimentally proved the above formation mechanism to be reasonable.

### 3:25 PM

**Anion-Exchange Separation in HCl Media for the Ultra-High Purification of Cobalt:** *Tamas Kekesi*<sup>1</sup>; Masahito Uchikoshi<sup>2</sup>; Kouji Mimura<sup>3</sup>; Minoru Isshiki<sup>3</sup>; <sup>1</sup>University of Miskolc, Miskolc, Egyetemvaros 3515 Hungary; <sup>2</sup>Fine Materials Corporation, Tagajo 985-0843 Japan; <sup>3</sup>Tohoku University, Inst. for Adv. Matls. Procg., Sendai 980-8577 Japan

Anion exchange in HCl media is considered an efficient alternative to the combination of the conventional purification methods. Anion-exchange distribution functions have been determined for cobalt and the main impurity elements by the technique of batch equilibration. Results were confirmed by spectrophotometric investigations and elution tests. Based on the new and the available distribution functions, combined with the assessment of thermodynamic stability, a procedure of anion exchange separation has been devised to eliminate virtually all the impurities from the cobalt-chloride solution. Separation of copper has been enhanced by the introduction of a preliminary step under reduced conditions. The rest of the impurities are eliminated in a second anion-exchange step applying rinsing and elution stages under oxidized conditions. The optimum parameters of the procedure have been determined according to performance characteristics (purification ratios, yields and volume efficiencies) derived from the analysis of elution curves obtained with laboratory scale ion-exchange columns. Special computer programs have been developed to facilitate thermodynamic simulation, analytical correction and data processing.

### 3:50 PM

**Morphological Characteristics of Nickel Particles Electrodeposited from Aqueous Solution:** *Guo Xueyi*<sup>1</sup>; Zhang Chuanfu<sup>2</sup>; Zhang Duomo<sup>2</sup>; Masazumi Okido<sup>3</sup>; Huang Kai<sup>2</sup>; Li Qihou<sup>2</sup>; <sup>1</sup>The University of Tokyo, Ctr. for Collaborative Rsrch., Komaba 4-6-1, Meguro-Ku, Tokyo 153-8505 Japan; <sup>2</sup>Central South University, Col. of Metallurg. Sci. & Eng., Changsha, Hunan 410083 China; <sup>3</sup>Nagoya University, Ctr. for Integrated Rsrch. in Sci. & Eng., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

In this study, the electrolytic nickel powder was deposited from the NiSO<sub>4</sub>-NH<sub>4</sub>Cl-NaCl-H<sub>3</sub>BO<sub>3</sub>-H<sub>2</sub>O solution. The morphological characteristics of the nickel particles electrodeposited from this aqueous solution were investigated. The effects of the electrolyte constituents, the parameters for the electro-deposition on the morphology of the nickel particles were addressed. It is concluded that not only the particle size, but also the morphology of the deposited nickel particles strongly depend on the electrolyte constituents and technical conditions. Especially, it is observed that the growth of the particle morphology is strongly related to the duration for electro-deposition. The ultra-fine nickel particles with flake, nodular or dendrite shape may be easily deposited by just controlling the time interval for particle growth. Further, the influences of various conditions on the particle morphology were explained, the growth mechanism of the particle electrodeposited from the solution was elucidated.

### 4:15 PM Break

### 4:25 PM Invited

**Detailed Mathematical Modeling of Liquid Metal Streamer Formation and Breakup:** David Dussault<sup>1</sup>; Adam C. Powell<sup>1</sup>; <sup>1</sup>Massachusetts Institute of Technology, Dept. of Matl. Sci. & Eng., 77 Massachusetts Ave., Rm. 4-117, Cambridge, MA 02139-4301 USA

A three-dimensional Cahn-Hilliard phase field model is formulated to describe transport-limited electrochemical reactions coupled with fluid flow in a metal reduction cell. When the reaction is limited by mass transfer of metal ions from the electrolyte to the cathode, the metal-electrolyte interface at the cathode exhibits a Mullins-Sekerka instability, leading to the growth of dendrite-like "streamers" of liquid metal into the electrolyte, which in turn significantly enhance the apparent mass transfer coefficient there. Model results for iron reduction from ferrous oxide in slag show formation of these streamers, and their breakup due to the instability of the cylindrical liquid-liquid interface. Although the double-layer is not included in this model, the related phenomenon of electrocapillarity is represented by a gradient penalty term which includes the electric potential gradient, such that interfacial energy is a function of the electric field normal to the interface.

### 4:55 PM Invited

**Purification of Leach Solutions by Direct Solvent Extraction:** *Chu Yong Cheng*<sup>1</sup>; Mark Urbani<sup>1</sup>; <sup>1</sup>AJ Parker Cooperative Research Centre for Hydrometallurgy/CSIRO Minerals, Australia, Conlon St, Waterford, PO Box 90, Bentley, WA 6982 Australia

The solvent extraction (SX) processes of the four nickel plants in Australia and the Goro SX process in New Caledonia were reviewed. The use of intermediate precipitation, solids/liquid separation and re-

leach in the three WA nickel plants and the use of Cyanex 301 for a direct solvent extraction (DSX) process in the Goro process make these processes complicated and costly in capital and operation. The research work carried out by the SX group at the AJ Parker Cooperative Research Centre for Hydrometallurgy/CSIRO Minerals has led to the invention of DSX processes to recover nickel and cobalt from leach solutions. The simplicity of the process flowsheets and the expected savings in capital and operating costs are the major advantages of the new DSX processes over the reviewed processes. By using a new synergistic organic system in semi-continuous tests with a pilot plant leach solution from BHP-Billiton Stainless Steel Materials (after iron precipitation), the metal values (Ni and Co) together with zinc and copper were separated from the major impurities (Mn, Mg and Ca, together with Cl) in the first SX circuit. The co-extracted manganese, magnesium and calcium were easily scrubbed out. After stripping, the metal values (Ni and Co) together with zinc and copper were concentrated, resulting in a much smaller second SX circuit and equipment in the down stream processes. The extraction and stripping kinetics of the metals with the new synergistic organic solution were very fast. Within 0.5 minutes, the extraction and stripping almost reached steady state. Semi-continuous test work with a synthetic leach solution, a cobalt pilot plant leach solution from Peko Rehabilitation Project Pty Ltd and a synthetic solution to simulate a concentrated solution from BHP-Billiton Stainless Steel Materials showed that manganese, calcium, copper and zinc can be effectively and efficiently separated from nickel, cobalt and magnesium by extraction, scrubbing and stripping. This led to the invention of another type of DSX process using D2EHPA to recover nickel and cobalt from leach solutions.

### 5:25 PM

**Nontoxic Method of Nickel/Cobalt/Copper Sulfides Precipitation as Rich Concentrates from Diluted Sulphate Solutions:** *M. I. Kalashnikova*<sup>1</sup>; Y. M. Shneerson<sup>1</sup>; M. V. Keskinova<sup>1</sup>; V. V. Chetvertakov<sup>1</sup>; <sup>1</sup>Norilsk Nickel RJS, Gipronickel Institute JS, Saint-Petersburg Russia

Results of investigations concerning precipitation of heavy non-ferrous metals from solutions using precipitators based on elemental sulphur and lime with gypsum transfer to a separate product are given.

### 5:50 PM

**The Polymorph Transformations of Antimony White:** Xiao Songwen<sup>1</sup>; Yan Xiaohui<sup>2</sup>; Xiao Xiao<sup>1</sup>; <sup>1</sup>Changsha Research Institute of Mining & Metallurgy, Lushanlanlu, Changsha, Hunan 410012 China; <sup>2</sup>Hunan Sunrise Nanometer Material Company, Ltd., Yuwanzheng, Changsha, Hunan 410014 China

On ground of the theoretical models of growth unites with coordination polyhedron structure of anion, the polymorph transformation mechanisms of antimony white Sb<sub>2</sub>O<sub>3</sub> in hydro-process was presented. The new findings had been verified in the commercial-scale test, and it showed that a small amount of tartrate ions in the solution was effective for the crystal transformation of antimony white in hydro-process.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Recycling, Waste Treatment and Environmental Issues III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday PM

Room: Leucadia

March 4, 2003

Location: San Diego Marriott Hotel

*Session Chairs:* Douglas Raymond Swinbourne, RMIT University, Sch. of Civil & Cheml. Eng, Melbourne, Victoria 3001 Australia; Venkoba Ramachandran, Ram Consultants, Scottsdale, AZ 85262 USA

### 2:30 PM Invited

**Treatment of Aqueous Effluents for Recovery and/or Removal of Metals in Non-Ferrous Metals' Industry—A Review:** *Venkoba Ramachandran*<sup>1</sup>; <sup>1</sup>Ram Consultants, 9650, E. Peregrine Pl., Scottsdale, AZ 85262 USA

In view of the increasing environmental regulations that have been promulgated in the last 30 years, non-ferrous smelters and refineries have learnt to handle effectively the process waste streams that need to be bled from the system for impurities' control. The cations of concern are copper, lead, zinc, cadmium, mercury, thallium, nickel, silver, sodium and potassium. Anionic species of arsenic and selenium also need to be addressed. Sulfates and chlorides-not a major problem at present- have come under scrutiny in the recent past. The current paper reviews several treatment options with reference to a)types of waste streams processed b)process chemistry c)discharge options and recovery of treated water and d)sludge disposal. The long term goal of any smelter and/or refinery should be to have zero liquid discharge from the plant. Methods to obtain zero discharge are discussed.

### 3:00 PM

**A Dynamic LCA Model for Assessing the Impact of Lead Free Solder:** *M. A. Reuter*<sup>1</sup>; *E. Verhoef*<sup>1</sup>; *A. Scholte*<sup>1</sup>; *G. Dijkema*<sup>1</sup>; <sup>1</sup>Delft University of Technology, Dept. of Appl. Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

While the importance of LCA to support decision-making, in particular to environmental impact assessment, is widely acknowledged, there is also some criticism. LCAs are very data intensive, which means the success of a study is strongly dependent on the availability of good data. Thus may explain why in many studies time dependence is neglected, and production of materials are considered individually. Although this may give rise to significant errors in calculated environmental impact, because of the interconnectedness and dynamics of systems considered. The carbon cycle, for example, is interlinked both via the non-hydrocarbon components of commercial plastics, such as chlorine and heavy metals, and via residues from refining and coals based operations. The production of one material, therefore, often is interrelated to and dependent on the consumption or generation of another. Most of the raw materials for silver production, for example, are not concentrated silver ores, but obtained as by-products of copper, steel and zinc production. When primary production of these material changes, silver production is affected. Similarly, in case outlets for arsenic cease to exist, primary production of copper, lead and zinc must be modified. Similar to this, the recovery of one material can interrelate to the recovery of another. The recycling of copper from mulling or the steel from cars also produces zinc. On that account, a dynamic, hierarchical model of a number of interconnected material cycles is developed. The model includes detailed models of the production and waste management stages to connect production or recovery of one material to the production of others. As the interconnection of metal production occurs at process level, modelling of the different production route involves considering the different types of production processes individually. The model is constructed on the basis of mass balances, in which the lower system levels represent increasing technical detail. Consistent with Reuter (1996) split factors, or recoveries, are used to model the processes. Data reconciliation is used on calculate the split factors from literature values on process feed, products and residue composition to ensure data quality. National, European or world production figures on process capacity can be used to calculate the relative contribution of processes. The model is set up dynamically. The continuous generation of new products, by-products, and material wastes result changes of the production network, e.g. the selection resources or suppliers employed, factory locations, innovation of facilities and products. In the model these changes can be considered, e.g. by changing the distribution of material flows over the different processes, or changing the split factors in time. The hierarchical structure allows matching the information needs of the different actors, supporting and/or coordinating decision-making processes in industry, SWM and governments. Municipal waste flows can be estimated from series of production data and assumption on delay of materials in the consumption phase. This allows for the evaluation of solid waste policy options in different dynamic scenarios with respect to the environment and resource depletion, but also the evaluation of the impact of lead-free soldering. The hierarchical structure allows In addition to the absolute environmental impacts, the model can be used to evaluate relative impact of policy, infrastructure or product design on the whole system as well.

### 3:25 PM

**Disposal Treatment of Alternative CFC Gas(C2H2F4) Using Chemical Reaction with Metal Compounds:** *Hideki Yamamoto*<sup>1</sup>; *Akihiro Kushida*<sup>1</sup>; *Norihiro Murayama*<sup>1</sup>; *Junji Shibata*<sup>1</sup>; <sup>1</sup>Kansai University,

Dept. of Cheml. Eng., Fac. of Eng., 3-3-35, Yamatecho, Suitashi, Osaka 564-8680 Japan

A new technology to make alternative CFC gas (C2H2F4:R-134a) used as refrigerant of an air cooling units or a refrigerators convert directly into a harmless substance have been established and new concept on the disposal treatment of global warming gas was presented. Reaction vessel made of Hastroy steel was applied to examine the chemical reaction of R-134a with metal chloride and metal oxides at the valuable experimental conditions. The effect of the kind of metal compound on the chemical reaction activity for the disposal treatment of R134-a gas was examined in this experiment. In the case of metal chloride(CaCl<sub>2</sub>, MgCl<sub>2</sub>), the beginning temperature of these chemical reactions are at 700K-770K and the reaction percentage of solid phase base is about 30-60%. Beginning temperature of the chemical reaction with metal oxide(CaO) is 820K, and the reaction percentage of solid phase base is about 60%. Experimental results verify that the chemical reactions can be take place at substantially lower temperature of 700 K-850K as compared with the combustion treatment method(1300K-1500K). Reaction product is mainly metal fluoride which is a harmless and a valuable chemical material as new resource. The other favorable characteristics are that the continuous treatment is possible at a low temperature under atmospheric pressure. Furthermore this process is compact, easily controllable and safely operable at low running cost. This paper concerns with a new harmless disposal treatment of toxic global warming gas.

### 3:50 PM

**Modelling and Control of Dioxin Formation During Iron Ore Sintering:** *Pengfu Tan*<sup>1</sup>; *Dieter Neuschütz*<sup>2</sup>; <sup>1</sup>Portovesme s.r.l., S.P.n.2-Carbonia/Portoscuso, Portoscuso 09010 Italy; <sup>2</sup>Rheinisch-Westfälische Technische Hochschule Aachen, Lehrstuhl für Werkstoffchemie, Aachen D-52056 Germany

In order to minimize dioxins and furans formation in iron ore sinter plants and to possibly avoid expensive end-of-pipe removal stages, thermodynamic calculations on the stability of PCDD/Fs have been combined with sinter process modelling by means of kinetic simulations and computational fluid dynamics. Three thermodynamics databases of PCDD/Fs, derived using the Group Additivity approach and two computational molecular modeling methods, MNDO and PM3, respectively, combined with the SGTE database have been used to model the PCDD/F formation and the PCDD/F isomer distributions in iron ore sintering. The results show very similar conditions for the PCDD/F formation using the different databases. The predicted isomer distributions of toxic PCDD/Fs have been compared with measured data from sinter plants, electrical arc furnaces, waste incinerators and wood burning furnaces. The calculated data using the database derived from the MNDO method show the best agreement with the industrial measurements. The thermodynamic calculations also show that the isomer distributions found in combustion processes are equilibrium values, while the concentration ratio of PCDDs and PCDFs in the wind boxes does not represent an equilibrium state. A CFD model of iron ore sintering was developed including the kinetics of 15 relevant chemical reactions with the aim of describing the chemical and the thermal processes of sintering and the gas flow patterns. On the basis of these informations possible pathways for the PCDD/F formation in sinter plants have been identified: Between charging zone and center part of the sinter bed, PCDD/Fs are formed below the hot zone, carried downwards with the gas and condensed in the cold zone. Transported to the discharge end with the solid mixture, they are again released into the gas phase when the flame front approaches the bottom of the bed. In addition, PCDD/Fs are formed in the last wind boxes when the hot off-gases cool down and reach the critical temperature range. Consequently, methods to reduce the dioxin formation reactions are proposed including inhibitor addition and off-gas quenching.

### 4:15 PM Break

### 4:35 PM Invited

**Behaviour of Thallium During Direct Lead Smelting—A Thermodynamic Viewpoint:** *Douglas Raymond Swinbourne*<sup>1</sup>; *Akira Yazawa*<sup>2</sup>; <sup>1</sup>RMIT University, Sch. of Civil & Cheml. Eng., PO Box 2476V, Melbourne, Victoria 3001 Australia; <sup>2</sup>Tohoku University, 16-32 Niizaka, Sendai 981-0934 Japan

Thallium is a minor element found in lead ores. The behaviour of thallium during lead smelting has become of much more interest recently due to the toxic effect it had on maintenance staff at one particular smelter. In this paper the behaviour of thallium will be examined using computational thermodynamics techniques for the case of direct smelting of lead concentrate by several generic technologies. Such methods have been pioneered by Prof. Yazawa to model many processes in extractive metallurgy. It will be shown that thallium

behaviour is strongly influenced by the presence or absence of certain secondary recycle materials in the charge and by the way in which the smelter offgases are handled.

### 5:05 PM

**Environmental Assessment of Imperial Smelting Process Practice in China:** *Guo Xueyi*<sup>1</sup>; Xiao Songwen<sup>2</sup>; Li Qihou<sup>2</sup>; Nie Zuoren<sup>1</sup>; Zhang Duomo<sup>2</sup>; Yamamoto Ryoichi<sup>1</sup>; <sup>1</sup>University of Tokyo, Ctr. for Collaborative Rsrch., Komaba 4-6-1, Meguro-Ku, Tokyo 153-8505 Japan; <sup>2</sup>Central South University, Col. of Metallurg. Sci. & Eng., Changsha, Hunan 410083 China

Imperial Smelting Process is one of important method to produce Zinc & Lead. Shaoguan Smelter in South China is a representative metallurgical plant to adopt ISP for the zinc and lead production with the annual production capacity of about 200 thousand tons. In this study, by analyzing the resource use, energy consumption and waste emission and disposal, the environmental burden of the ISP practice in this smelter was addressed, the impact assessment was conducted quantitatively by applying some environmental indicators, and further the approaches for improving the resource & energy use efficiency as well as releasing the environmental burden were proposed.

### 5:30 PM

**Use of Solid Hematite to Fix Arsenic Contained in a Gas Phase:** *A. Gonzalez*<sup>1</sup>; E. Balladares<sup>1</sup>; R. Parra<sup>1</sup>; M. Sánchez<sup>1</sup>; <sup>1</sup>Universidad de Concepción, Edmundo Larenas 270, Casilla, Concepción 53-C Chile

Arsenic is one of the main contaminants presents in copper mining resources today and its abatement represents a challenge for metal extraction in the future, particularly under the strong environmental requirements in a global community. The possibility to form ferric arsenate directly from a gas phase by means of a heterogeneous reaction between an arsenic gas bearing and iron oxide was studied at laboratory scale. A thermodynamical analysis for the system Fe-As-O-S has been initially made, in order to obtain the stability conditions for the ferric arsenate or other  $Fe_xAs_yO_z$  type compounds. Experiments were made using an hematite sample suspended from a thermogravimetric device, inside a vertical furnace. Gas As<sub>4</sub>O<sub>6</sub> generated from solid As<sub>2</sub>O<sub>3</sub> were passed through the iron oxide sample and its instantaneous weight changes was recorded directly in a computer. A kinetic study for the As<sub>4</sub>O<sub>6</sub> volatilization was made, which shows chemical control between 300 and 600°C, and with an apparent activation energy of around 14 Kcal/mol As<sub>2</sub>O<sub>3</sub>. Samples after reactions were chemically and by XRD analysed. Arsenates detected corresponds to complex compounds. Results shows that formation of compounds depend on temperature and oxygen content of the gas phase. Kinetic for iron arsenates formation is slow, reaching an arsenic capture of 6% after 80 minutes of reaction when an oxygen content of 50% is fed continuously at 800°C. Experiences made at the same temperature but under higher oxygen content in a closed reactor, allowed arsenic capture close to 60%. For higher temperatures capture is notoriously lower.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: General III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee: See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Tuesday PM  
March 4, 2003

Room: Point Loma  
Location: San Diego Marriott Hotel

*Session Chairs:* Chikabumi Yamauchi, Chubu University, Grad. Sch. of Eng. & Sch. of Eng., Aichi-ken 487-8501 Japan; David G.C. Robertson, University of Missouri-Rolla, Dept. of Metallurg. Eng., Rolla, MO 65401 USA

### 2:30 PM Keynote

**The Chemistry of Fuming Zinc from Oxide Slags Using Coke:** *David G.C. Robertson*<sup>1</sup>; Dhiren K. Panda<sup>2</sup>; Adrian C. Deneys<sup>3</sup>; <sup>1</sup>University of Missouri-Rolla, Dept. of Metallurg. Eng., Rolla, MO 65401 USA; <sup>2</sup>Nucor-Yamato Steel, Blytheville, AR 72315 USA; <sup>3</sup>Praxair, Inc., Indianapolis, IN 46222 USA

The key reaction in zinc fuming is  $ZnO(\text{in slag}) + CO = Zn(g) + CO_2$ . This paper includes the results of experiments carried out by the authors. In the first series of experiments it was shown that the reaction  $2FeO + ZnO = Fe_2O_3 + Zn(g)$  does not occur at an appreciable rate. In the second series it was shown that zinc oxide is not reduced unless a reductant has been added. A third series of experiments was carried out with excess coke. The kinetics of zinc oxide reduction were found to be independent of the zinc oxide concentration, but increased with increasing basicity, and temperature. The presence of high concentrations of FeO in the slag is also known to increase the rate. We propose that, in our work, the kinetics were controlled by a chemical step, namely the rate of desorption of an adsorbed CO<sub>2</sub> species.

### 3:00 PM

**Effect of Ultrasonic Wave Irradiation on the Electrical Conductivity of Pure and Sodium Doped Sulfur Melts:** *Nobuaki Sato*<sup>1</sup>; Rajmund Michalski<sup>2</sup>; Takeo Fujino<sup>3</sup>; Yoshio Waseda<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan; <sup>2</sup>Polish Academy of Science, Inst. of Environml. Eng., Skrodowska-Curie 34 St., Zabrze 41-819 Poland; <sup>3</sup>Tohoku University, Inst. for Adv. Matls. Progc., 19-14 Higashioshima, Hitachinaka 312-0042 Japan

Sulfur melt is expected to have a potential use in the materials synthesis field as a molten process, such as a low temperature synthesis of mixed sulfides. If the adiabatic property of the sulfur is improved to have a relatively high conductivity by the irradiation of ultrasonic waves, it would extend to the electrochemical process. In this paper, the electrical conductivity,  $\sigma$ , of pure and sodium doped sulfur melts was measured in the presence of ultrasonic waves from 433 to 573 K by the two probe method using ultra high resistor meter. The  $\sigma$  value of the pure sulfur melt with irradiation was jumped at around 443 K by the order of 10<sup>2</sup> and then monotonically increased from 10<sup>-5</sup> to 10<sup>-4</sup> Scm<sup>-1</sup> with increasing temperature. The addition of sodium metal to the sulfur melt was proved to be more effective for jumping the  $\sigma$  value of the melt to an acceptable level when ultrasonic wave was irradiated.

### 3:25 PM Invited

**Mathematical Modeling of Phase Interaction Taking Place During Fusion Welding Processes:** *Michael Zinigrad*<sup>1</sup>; Vladimir Mazurovsky<sup>1</sup>; Alexander Zinigrad<sup>1</sup>; <sup>1</sup>College of Judea and Samaria, Science Park, Ariel 44837 Israel

The quality of metallic materials depends on their composition and structure and these are determined by various physico-chemical and technological factors. To effectively prepare materials with required composition, structure and properties is necessary to carry out research in two parallel directions: 1. Comprehensive analysis of thermodynamics, kinetics and mechanisms of the processes taking place at the solid-liquid-gaseous phase interface during welding processes; 2. Development of mathematical models of the specific welding technologies. We have developed unique method of mathematical modeling of phase interaction at high temperatures. This method allows us to build models taking into account: thermodynamic characteristics of the processes, influence of the initial composition and temperature on the equilibrium state of the reactions, kinetics of heterogeneous processes, influence of the temperature, composition, hydrodynamic and thermal factors on the velocity of the chemical and diffusion processes. The model can be implemented in optimization of various technological processes in welding, surfacing, casting as well as in manufacturing of steels and non-ferrous alloys, materials refining, alloying with special additives, removing of non-metallic inclusions.

### 3:50 PM

**Green Technology to Recovery Value Metal Compounds from Molten Slags:** *Zhitong Sui*<sup>1</sup>; Li Zhang<sup>1</sup>; Taiping Lou<sup>1</sup>; Zhida Sui<sup>1</sup>; <sup>1</sup>Northeastern University, Sch. of Matls. & Metall., Shenyang 110006 China

Based on several case studies in precipitating behavior of value metal compounds (VMC) in molten slags a green technology to recovery VMC from molten slags is proposed, in which three steps are involved: (1) The selective concentrating of dispersed VMC into the designed mineral phase in molten slag; (2) The selective coarsening of the designed mineral phase to critical grain size in molten slag; (3) The selective separating of the grown mineral phase in solidified slag from tailing by dressing or hydrometallurgy processes. The features of the technology are economic, clean, intensive and comprehensive. The utilization of recovered VMC such as Titanium, Boron, Vanadium,

chromium and Iron compounds was summarized as examples of technology application. It was confirmed by experiments that the precipitating of the designed mineral phases like Perovskite ( $\text{CaTiO}_3$ ), Suanite ( $2\text{MgO} \cdot \text{B}_2\text{O}_3$ ), Spinel ( $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ ) and Magnetite ( $\text{Fe}_3\text{O}_4$ ) in molten slags are obviously affected by operation factors such temperature, chemical composition, heat-treatment, additives and so on. The precipitating kinetics and mechanism of VMC from molten slags during solidification processes were also investigated.

#### 4:15 PM Break

#### 4:35 PM Keynote

**Progress and Problems in the Simulation of Non-Ferrous Extraction Processes:** *Arthur E. Morris*<sup>1</sup>; <sup>1</sup>Thermart Software, 12102 Calle de Maria, San Diego, CA 92128-2720 USA

Fifty years ago when Professor Yazawa began his career, the field of process simulation and modeling was in its infancy. Since then, tremendous progress has been made in our ability to model metal production flowsheets from mine to refined metal. This progress has come about by parallel developments in basic understanding of process chemistry and in computational techniques. This paper will review the progress made in process understanding and modeling in lead, zinc, and copper metallurgy from its inception to the present, and the role of Professor Yazawa's work in furthering this progress. Specific examples will be given for the sintering of lead concentrates, slag fuming, zinc concentrate roasting, flash smelting of copper, and pyro-extraction of zinc. Factors limiting further progress will be described.

#### 5:05 PM

**The Experiment on Reducing-Matte Smelting of Jamesonite Concentration:** *Tang Chaobo*<sup>1</sup>; *Tang Motang*<sup>1</sup>; *Yao Weiyi*<sup>1</sup>; <sup>1</sup>Central South University, Dept. of Metall., Yuelunanlu, Changsha, Hunan 410083 China

The reducing-matte smelting is a new pollution-free metallurgy technique. In the process pyrite cinder or ferric oxide ore reacts with non-ferrous metal sulphide and produce metal. In this paper, the reducing-matte smelting of jamesonite concentrate has been conducted, and the influences of temperature, amount of pyrite cinder and amount of additive on the smelting process have been studied. Under the optimum technical conditions, the direct recovery ratio of antimony and lead are 83.26% and 68.5%. The ratio of fixed sulfur is 98.97%. It shows that this method is feasible and pollution-free of sulfur dioxide. But the distribution ratio of lead and silver in ferrous matte is 15% and 30%, therefore how to recover lead and silver economically and effectively from ferrous matte is still a problem to be solved.

#### 5:30 PM

**Melt Atomisation—The Bridge from Pyro- to Hydro-Metallurgy:** *J. J. Dunkley*<sup>1</sup>; *D. Norval*<sup>2</sup>; <sup>1</sup>Atomising Systems, Ltd., Sheffield S9 1EW England; <sup>2</sup>Bateman Pty, Johannesburg S. Africa

Recent years have seen the increased use of hydrometallurgy in the smelting and refining of metals. However this is often used as a final refining step, following an initial pyrometallurgical smelting process. Huge amounts of material are produced as melts which have to be cast, comminuted, and taken up into solution or leached. A common method is to granulate the melt and then grind it. In the case of metallic melts this can be difficult or unfeasible due to the ductility of the granulated particles. Water atomisation is capable of replacing the granulation and grinding stages with a single process step that can process in excess of 30t/hour of melt into particles as fine as 50 microns. Applications in operation in Co, Cu, Ni, Ag, Au, Pt and Rh refining are discussed together with potential applications in copper smelting.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Iron and Steel Making Fundamentals I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday AM

Room: Leucadia

March 5, 2003

Location: San Diego Marriott Hotel

*Session Chairs:* V. Sahajwalla, The University of New South Wales, Sch. of Matls. Sci. & Eng., Sydney, NSW Australia; Takashi Nakamura, Tohoku University, Dept. of Metall. Grad. Sch. of Eng., Sendai Japan

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#### 8:30 AM Invited

**A Basic Study on the Effective Utilization of Chromium-Containing Steel Slag:** *Etsuro Shibata*<sup>1</sup>; *Takashi Nakamura*<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 1,1 Katahira, 2-Chome, Aobaku, Sendai 980-8577 Japan

The solubility of chromium oxide and valance of chromium in slag are important to consider how to utilize effectively the chromium-containing slag. Those experimental data of various types of slag cited in literatures were arranged using optical basicity, and the effects of oxygen potential and slag composition were investigated. The saturated solubility of chromium oxide and the ratio of  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$  tend to decrease with increase in optical basicity of slag at the oxygen potential below  $10^{-5}$  atm. On the other hand, at the oxygen potential of 0.21 atm, the saturated solubility and the ratio of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  tend to increase with increase in optical basicity. For a practical approach to reduce chromium in stainless steel slag and simultaneously recover chromium as a ferroalloy, the direct smelting reduction of chromium oxide in molten slag using some reductant was also investigated using a small furnace.

#### 8:55 AM Invited

**Kinetics of Carbon Injection into Metallurgical Slag:** *F. Ji*<sup>1</sup>; *M. Barati*<sup>1</sup>; *K. S. Coley*<sup>1</sup>; *G. A. Irons*<sup>1</sup>; <sup>1</sup>McMaster University, McMaster Steel Rsrch. Ctr., Hamilton, Ontario L8S 4L6 Canada

Carbon injection into metallurgical slags is important in EAF steel-making for slag foaming and in nonferrous slag cleaning. The current publication presents kinetic data for coal injection into electric arc furnace slags to draw some general conclusions about the interaction between injected carbon and metallurgical slags. Coal particles were injected into EAF slags and the kinetics were followed by gas and slag analysis. The results were analyzed, in terms of fundamental rate equations for each possible reaction step, as a function of temperature and slag composition.

#### 9:20 AM

**Semi-Stochastic Optimization of Chemical Composition of High-Temperature Austenitic Steels for Desired Mechanical Properties:**

*George S. Dulikravich*<sup>1</sup>; *Igor N. Egorov*<sup>2</sup>; *Vinod K. Sikka*<sup>3</sup>; *Govindarjan Muralidharan*<sup>3</sup>; <sup>1</sup>University of Texas at Arlington, Mech. & Aeros. Eng. Dept., Multidisciplinary Anal., Inverse Design & Optimization (MAIDO) Prog., UTA Box 19018, Arlington, TX 76019 USA; <sup>2</sup>IOSO Technology Center, Milashenkova 10-201, Moscow 127322 Russia; <sup>3</sup>Oak Ridge National Laboratory, Matls. Procg. Grp., PO Box 2008, MS6083, Metals & Ceram. Div., Oak Ridge, TN 37831-6083 USA

The methodology for steel optimization subject to several simultaneous objectives consists in organization an iterative optimized experiment. The result of these studies is the Pareto-optimal set of steel compositions that simultaneously optimizes the chosen objectives. The multi-objective optimization algorithm is based upon the use of a response surface that is created from the available experimental data with the help of radial-basis functions and artificial neural networks. During the conduct of research the information is being stored con-

cerning the properties of steel in the vicinity of the Pareto set. This allows us to improve the accuracy of the results. As the independent design variables we considered the percentage of following components: C, Mn, Si, Ni, Cr, N. Ranges of their variation were set in accordance with lower and upper bounds of the available set of experimental data. As the main optimization objective we considered the strength of the H-type steel after 100 hours under the temperature of 1800F. Other objectives have been chosen based on the necessity to reduce the cost of the steel. In this work, the additional three objectives were to simultaneously minimize the percentages of Mn, Ni, Cr. Thus, the multi-objective optimization problem had 6 independent design variables and 4 objectives. We defined the desirable number of Pareto optimal solutions as 10 points. Every iteration of this methodology results in a formulation of a set of steel compositions, which are Pareto optimal and need experimental evaluations to obtain the true values of the objectives.

#### 9:45 AM

**"In-Situ" Observation of Iron Carburization During Smelting Reduction:** *Ko-ichiro Ohno*<sup>1</sup>; Tetsuya Nagasaka<sup>2</sup>; Mitsutaka Hino<sup>2</sup>; <sup>1</sup>Tohoku University, Dept. of Metall., Aza-Aoba 02, Aramaki, Aoba-ku, Sendai 980-8579 Japan; <sup>2</sup>Tohoku University, Dept. of Metall., Grad. Sch. of Eng., Aoba-yama 02, Sendai 980-8579 Japan

It was recently recognized that the reduction, melting of iron and slag separation in the composite of granular iron ore and coal are completed in a very short period of about 10 minutes when the composite is heated rapidly up to approximately 1673K. Utilization of these phenomena is attempted for new iron-making process. The mechanism of iron ore reduction and iron-slag separation during rapid heating has not yet been realized, and the fundamental research has just been started. Carburization of the reduced iron is regarded as an important factor in this process. In the present work, the composite was prepared from four kinds of coal or graphite and electrolytic iron powder. The temperature at which liquid were formed and iron was carburized was monitored at various heating speeds. Direct observation of smelting reduction behavior was made by a laser microscope combined with the infrared image heating furnace to clarify the effect of molten ash on iron carburization. The meltdown temperature of composite fell as melting temperature of coal ash fell. From the observed result, it was presumed that liquid formation in composite triggered carburization of iron. Carburization mechanism during smelting reduction was considered as follows. When slag containing iron oxide melted down and contacted with carbon, iron oxide in slag was reduced and metallic iron particle was formed and carburization of the iron particle occurred simultaneously at slag-carbon interface. Carburized iron particle was carried from slag-carbon to slag-iron interfaces due to slag convection flow caused by the difference of interface tension between carbon-slag and iron-slag interfaces. Repeating the above-mentioned process continuously carburized the reduced iron.

#### 10:10 AM Break

#### 10:20 AM Invited

**Fundamental Investigation of Basic Mechanisms of Carbon Dissolution in Molten Iron:** *V. Sahajwalla*<sup>1</sup>; R. Khanna<sup>1</sup>; <sup>1</sup>The University of New South Wales, Sch. of Matls. Sci. & Eng., Sydney, NSW 2052 Australia

Based on experimental and computer simulation results from our group, we report a systematic, atomic level analysis of carbon dissolution from carbonaceous materials in molten iron. Experimental results were obtained using carbon dissolution studies, wetting, XRD and FESEM investigations, and Monte Carlo simulations on Graphite/Fe-C-S system. Three basic mechanisms, namely carbon atom dissociation rate, interfacial phenomena and mass transfer in the melt were found to be responsible for the overall dissolution process. While mass transfer in the melt is governed by the concentration gradients, impurities such as sulphur and temperature, sulphur and oxide impurities present in ash play a significant role in the interfacial phenomena. Carbon atom dissociation kinetics depends strongly on the degree of long-range order of carbonaceous materials and is an important rate controlling mechanism in the overall dissolution kinetics of less ordered forms of carbon. A systematic comparison of dissolution rates for a variety of coals, cokes, chars, natural and synthetic graphite has been carried out in an attempt to identify rate-controlling mechanisms. The structure of the carbonaceous material appears to be an important underlying factor in carbon dissolution.

#### 10:45 AM Invited

**Dissolution of Alumina Particles in CaO-Based Fluxes:** *W. D. Cho*<sup>1</sup>; Peter Fan<sup>1</sup>; <sup>1</sup>University of Utah, Dept. of Metallurg. Eng., Salt Lake City, UT 84112 USA

The slag chemistry in steel processing plays an important role in terms of the removal of impurities including alumina particles. In the present study, the dissolution of solid alumina particles in CaO-based fluxes at the temperatures between 1450 and 1550°C has been investigated to determine dissolution kinetics and mechanism. Alumina particles were added directly in the slags and the size of alumina particles was measured as a function of time using optical and scanning electron microscopes. The dissolution rate has also been obtained as a function of SiO<sub>2</sub>, CaF<sub>2</sub>, MgO and MnO contents in the slags. The diffusion boundary layer between alumina and bulk slag phase has been observed and analyzed using SEM and EDX. In addition, some experiments have been performed for the dissolution of alumina in BaO-based fluxes.

#### 11:10 AM

**The Effect of MgO and Al<sub>2</sub>O<sub>3</sub> Additions on the Liquidus for the CaO-SiO<sub>2</sub>-FeOx Systems at Various Partial Pressure of Oxygen:** Hisao Kimura<sup>1</sup>; *Fumitaka Tsukihashi*<sup>2</sup>; <sup>1</sup>The University of Tokyo, Grad. Sch. of Eng., 7-3-1 Hongo, Bunkyo, Tokyo 113-8656 Japan; <sup>2</sup>The University of Tokyo, Grad. Sch. of Frontier Sci., 7-3-1 Hongo, Bunkyo, Tokyo 113-0033 Japan

Phase diagrams for the CaO-SiO<sub>2</sub>-FeOx-MgO, Al<sub>2</sub>O<sub>3</sub> systems are necessary for the analysis of copper smelting reaction and sintering process of iron ore. The effect of MgO and Al<sub>2</sub>O<sub>3</sub> addition on the liquidus of phase diagram for the CaO-SiO<sub>2</sub>-FeOx systems at low oxygen partial pressure was observed. The liquid phase area was changed by the addition of MgO and Al<sub>2</sub>O<sub>3</sub> with changing oxygen partial pressure from 10<sup>-8</sup> to 10<sup>-3</sup> atm at 1573K. The effect of Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio on the melting mechanism is discussed.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Elemental Losses and Distributions

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPM/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday AM

Room: Solana

March 5, 2003

Location: San Diego Marriott Hotel

*Session Chairs:* Yoichi Takeda, Iwate University, Fac. of Eng., Morioka 020-8551 Japan; Kimio Itagaki, Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., Sendai, Miyagi 980-8577 Japan

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#### 8:30 AM Keynote

**Distribution of Minor Elements in Sulfide Smelting:** *Kimio Itagaki*<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577 Japan

Various kinds of molten sulfide systems of Cu<sub>2</sub>S-FeS, Ni<sub>3</sub>S<sub>2</sub>-FeS, Ni<sub>3</sub>S<sub>2</sub>-Cu<sub>2</sub>S-FeS, ZnS-Cu<sub>2</sub>S, PbS-Cu<sub>2</sub>S, Ni-S and Pb-S were equilibrated with molten FeOx-SiO<sub>2</sub>, FeOx-CaO and Al<sub>2</sub>O<sub>3</sub>-CaO based slags in a magnesia crucible under controlled partial pressures of SO<sub>2</sub>, O<sub>2</sub> and S<sub>2</sub> to determine the distribution ratios of some valuable (Ag, Au, Co, Ni etc.) and detrimental (Pb, As, Sb, Bi etc.) minor elements in smelting various sulfide concentrates. The experimental results were analyzed on the basis of thermodynamics and the effects of partial pressures of oxygen and sulfur as well as slag basicity were discussed in this study.

#### 9:00 AM

**Thermodynamic Evaluation of Arsenic and Antimony on the Bessemer Matte and Calcium Ferrite Slag:** *Jonkion M. Font*<sup>1</sup>; Mitsuhsa Hino<sup>2</sup>; Kimio Itagaki<sup>2</sup>; <sup>1</sup>The University of Alabama, Dept. of Metallurg. & Matls. Eng., PO Box 870202, Tuscaloosa, AL 35487-0202 USA; <sup>2</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., Sendai, Miyagi 980-8577 Japan

Due to the known disadvantages of the use of iron silicate slag in the nickel converting stage, i.e., high metal losses, high magnetite content, and low fixation of impurities in the slag, the development of the new proposed "ferrous calcium silicate" slag for smelting and converting processes of nickel is very promising. Hence, considering the successful experimental results of using CaO base slag for the nickel smelting process, a study based on a detailed comparison for the phase equilibrium, and the minor elements distribution between the Ni<sub>3</sub>S<sub>2</sub>-FeS matte with either FeO<sub>x</sub>-CaO or FeO<sub>x</sub>-SiO<sub>2</sub> base slag was investigated. The main results are summarized as: no difference in the nickel losses between both slags was found at high nickel content in the matte, and the fractional distribution analysis for arsenic and antimony pointed out their preferential fixation in the calcium ferrite slag rather than in the iron silicate slag. The technical feasibility of using calcium ferrite slag in a converting process of the Bessemer matte will have a prominent future for the nickel industry when the energy and pollution issues are taken into account.

#### 9:25 AM

**Thermodynamics of PbO, ZnO and CuO<sub>0.5</sub> in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Melts:** *Takaaki Ishikawa*<sup>2</sup>; Kenji Matshuzaki<sup>3</sup>; Takayuki Tsukada<sup>1</sup>; Kimihisa Ito<sup>1</sup>; <sup>1</sup>Waseda University, Matls. Sci. & Eng., 3-4-1, Okubo, Shinjuku-ku, Tokyo 169-8555 Japan; <sup>2</sup>Chiba Prefectural Machinery & Metallurgy Research Institute, Chiba 263-0016 Japan; <sup>3</sup>Mitsui Mining & Smelting, Rsrch. Ctr., Saitama 362-0021 Japan

The distribution equilibria of lead, zinc and copper between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> melts and liquid copper were measured at 1623K under a controlled H<sub>2</sub>-CO<sub>2</sub> atmosphere. The distribution ratios were plotted against the oxygen partial pressure, and reasonable oxide forms dissolved in the melts were estimated from the slopes of the plots. The activity coefficients of lead oxide (PbO), zinc oxide (ZnO) and cuprous oxide (CuO<sub>0.5</sub>) increased with increasing slag basicity, defined by XCaO/XSiO<sub>2</sub>. The temperature dependence of the activity coefficients was also measured.

#### 9:50 AM

**Distribution of Minor Elements Between Ni-S Melt and Al<sub>2</sub>O<sub>3</sub>-CaO-MgO Slag at 1873 K:** *Hector Mario Henao*<sup>1</sup>; Mitsuhiro Hino<sup>1</sup>; Kimio Itagaki<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls. (IMRAM), 1-1 Katahira, 2-Chome, Sendai, Miyagi 980-8577 Japan

To provide thermodynamic data for converting the nickel matte to liquid nickel, distribution ratios of some minor elements (Au, Ag, Cu, Co, Fe, P) between the Ni-S alloy and the Al<sub>2</sub>O<sub>3</sub>-CaO-MgO slag in a magnesia crucible were determined at 1873 K under controlled PSO<sub>2</sub> of 10.1 kPa and PO<sub>2</sub> in a range between 8.0 and 0.1 Pa by using CO-CO<sub>2</sub>-SO<sub>2</sub> gas mixtures. It was found that the distribution ratios, L<sub>X</sub><sup>S/Ni</sup>, defined by (mass%X in slag)/(mass%X in alloy), for P, Fe are larger than unity, while less than unity for Au, Ag, Cu, Co.

#### 10:15 AM Break

#### 10:25 AM Keynote

**Thermodynamic Evaluation of Copper Loss in Slag Equilibrated with Matte:** *Yoichi Takeda*<sup>1</sup>; <sup>1</sup>Iwate University, Fac. of Eng., Ueda 4-3-5, Morioka 020-8551 Japan

Main focus is the determination of copper solubility in SiO<sub>2</sub>-CaO-FeOx slag equilibrated with matte under specified SO<sub>2</sub> atmosphere. A classical thermodynamic model postulating CuO<sub>0.5</sub> and CuS<sub>0.5</sub> molecules applies to calculate copper solubility in slag. A large number of experiments provide proper parameters: activity coefficients of copper oxide and sulfide, oxygen and sulfur potentials and activity of copper in the slag-matte system. Copper loss, that is function of copper solubility and slag volume, in the silica saturated SiO<sub>2</sub>-FeOx binary slag is minimally equilibrated with less than 66% copper matte while copper loss in the 50% FeOx-SiO<sub>2</sub>-CaO is minimally equilibrated with over 66% copper matte. This slag composition has potential for continuous copper converting, direct copper production or high-grade matte production.

#### 10:55 AM Invited

**Copper Losses in Copper Smelting Slags:** *Ivan Imris*<sup>1</sup>; <sup>1</sup>Technical University of Kosice, Dept. of Power Eng., Fac. of Mechl. Eng., Letna 9, Kosice 041 87 Slovak Republic

The common problem of new and conventional technology of copper production is the copper losses in the slags, which may be divided into mechanical and physico-chemical losses. In the first group can be included particles of mechanically entrained or floated undissolved matte particles which coexist with slag. On the other hand, the physico-chemical losses are caused by solubility of copper in the slag in the form of sulphide and oxide. The copper losses in the slags from different processes has been predicted by calculation from thermodynamic data and compared with those determined by micro-

scopic examination and quantitative electron microprobe analysis. Depending on the forms of copper losses in the slags the reduction of copper losses in the slag or the slag cleaning process could be suggested.

#### 11:20 AM

**Distribution Behavior of Arsenic, Antimony and Bismuth:** *Supachai Surapunt*<sup>1</sup>; Nozomu Hasegawa<sup>2</sup>; <sup>1</sup>Thammasat University, Fac. of Eng., 99 Phaholyothin Rd., Klong-Luang, Pathumthani 12121 Thailand; <sup>2</sup>Naoshima Smelter and Refinery, Mitsubishi Metal Corp., Naoshima, Kagawa Japan

The distribution behavior of VA minor elements (As, Sb and Bi) in the smelting stage of the Mitsubishi process were evaluated thermodynamically based on thermodynamic data and operating data by using the method of calculation proposed by Itagaki and Yazawa. The fractional distributions between the gas, slag and matte phases considered as the degree of vapor saturation of 0.8 are as follows: 53.8, 27.2 and 19% for As, 23.6, 56.6 and 19.8% for Sb, and 91.3, 1.1 and 7.6% for Bi, respectively. Arsenic is mostly distributed to the gas and slag phases. It is effectively eliminated by volatilizing and slagging. Antimony is mainly in the slag phase which is suitably removed by slagging. Bismuth is easily vaporized to gas phase. The degree of vapor saturation has a large effect on the distribution behaviors of the three elements between the three phases. The amount of a minor element in the charge has an effect on the distribution of As but no effect on the distributions of Sb and Bi. Increasing matte grade and temperature results in the change of distributions for As and Sb, significantly. The change in the distribution ratio between slag and matte phases also considerably affects the distributions of As and Sb. The distribution behavior of Bi is not significantly changed by the change in matte grade, temperature and distribution ratio.

#### 11:45 AM

**The Influence of Reverb Slag Composition on Copper Losses:** *Natasa Mitevska*<sup>1</sup>; *Zivan D. Zivkovic*<sup>1</sup>; <sup>1</sup>Copper Institute, Zeleni bulevar 35, Bor 19210 Yugoslavia

The statistical analysis of the slag composition influence on copper losses to discard slag in the reverberatory furnaces No. 1 and No. 2 in the RTB BOR, Copper Smelter and Refinery (Yugoslavia) is presented in this paper. The model for the slag basicity calculation is determined, and connected to the copper distribution coefficients between the matte and slag phase. The influence of all components on the slag structure is also illustrated.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Materials Processing Technologies: General I

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday AM

Room: Point Loma

March 5, 2003

Location: San Diego Marriott Hotel

*Session Chairs:* Toshiyuki Kozuka, Kumamoto University, Dept. of Matls. Sys., Kumamoto 860-8555 Japan; Y. B. Hahn, Chonbuk National University, Chonju 561-756 Korea

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#### 8:30 AM Invited

**Fabrication of Blue Light-Emitting Diodes Using GaN-Based Multiple Quantum Wells Grown by Metal Organic Chemical Vapour Deposition:** *Yoon-Bong Hahn*<sup>1</sup>; Rak-Jun Choi<sup>1</sup>; Hyung Jae Lee<sup>1</sup>; <sup>1</sup>Chonbuk National University, Sch. of Cheml. Eng. & Tech., Semiconductor Physics Rsrch. Ctr., 664-14 Duckjin-Dong 1 Ga, Chonju 561-756 Korea

Gan-based blue light emitting diodes (LEDs) were fabricated by utilizing nanoscale triangular- and rectangular-type multiple quantum wells and their characteristics were compared in terms of structural, electrical and optical properties. Optimization of the LED fabrication process was also investigated by minimizing a plasma-induced damage. The InGaN/GaN multiple quantum wells (MQWs) were grown by a low-pressure metalorganic chemical vapour deposition method. The size of quantum dots formed in the active layer of InGaN was in a range of 2 to 50 nm, and the dots in the triangular QWs showed very uniform spatial distribution compared to those in the rectangular QWs. Both photoluminescence (PL) and electroluminescence (EL) showed higher emission and smaller full-width at half maximum in QWs and LED structures with triangular QWs than those with rectangular QWs. Especially, EL spectrum as a function of injection current showed that the peak energy is nearly independent of the injection current in the triangular-QW based LEDs. In the course of LED fabrication a physical degradation of sidewall along with rough surface morphology of n-GaN caused by increased ion scattering induced the deterioration of forward and reverse voltages. It was found that the turn-on voltage is sensitive to the surface roughness of the etched n-GaN and the breakdown voltage is strongly affected by the sidewall contamination. Annealing under nitrogen after the mesa etching improved the electrical properties of the InGaN/GaN MQW LEDs.

#### 9:00 AM

**Sintering of Pb{Zr,Ti,(Mg1/3Nb2/3)}O<sub>3</sub> Ceramics by Spark Plasma Sintering and their Compositional Distribution:** Kazuyuki Kakegawa<sup>1</sup>; Satoru Sawahara<sup>2</sup>; Naofumi Uekawa<sup>3</sup>; <sup>1</sup>Chiba University, Grad. Sch. of Sci. & Tech. & Dept. of Mat. Tech., Fac. of Eng. & Ctr. for Frontier Elect. & Photonics, 1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522 Japan; <sup>2</sup>Chiba University, Grad. Sch. of Sci. & Tech., Chiba 263-8522 Japan; <sup>3</sup>Chiba University, Dept. of Mat. Tech., Fac. of Eng. & Ctr. for Frontier Elect. & Photonics, Chiba 263-8522 Japan

Both sintering and homogenization of ceramic solid solutions are the result of diffusion during the heating at high temperatures. Thus homogenization generally accompanies with sintering. It is a normal fact that distribution of composition decreases as the sintered density of the sample increases. We found an interesting fact that dense sintered body could be obtained with almost no change in the compositional distribution, when spark plasma sintering (SPS) method was employed. This paper shows such results in Pb{Zr,Ti,(Mg1/3Nb2/3)}O<sub>3</sub> solid solution. The change in the compositional distribution of the sintered body by SPS was compared with that by the normal sintering. By normal sintering, the compositional distribution decreased as the sintered density increased as normally expected. On the contrary, the compositional change by SPS was much smaller than that by the normal sintering. This sintering characteristic of SPS enabled a fabrication of sintered material having a desired compositional distribution.

#### 9:25 AM

**Mg Alloy Composite Materials with Solid-State Synthesized Mg<sub>2</sub>Si Dispersions:** Katsuyoshi Kondoh<sup>1</sup>; Wenbo Du<sup>1</sup>; Ritsuko Tsuzuki<sup>1</sup>; <sup>1</sup>The University of Tokyo, Rsrch. Ctr. for Adv. Sci. & Tech. (RCAST), 4-6-1, Komaba, Meguro-ku, Tokyo 153-8904 Japan

The synthesis processing of Mg<sub>2</sub>Si or Mg<sub>2</sub>Si/MgO at lower temperature from the elemental magnesium alloy chips and Si or SiO<sub>2</sub> powder mixture was established via the cyclic plastic working based on Powder Metallurgy (P/M) process, which is effective on the mechanical breakage of MgO surface films preventing from the solid-state reaction between Mg and Si powder. The Mg<sub>2</sub>Si grain of 200-500nm is extremely fine, compared to that via the conventional casting process, because of not coarsening during the solid-state synthesis of Mg<sub>2</sub>Si. By using in-situ forming process of Mg<sub>2</sub>Si via the cyclic plastic working, the magnesium composite material with Mg<sub>2</sub>Si/MgO dispersions, which particle size was less than 1-3µm, was developed. For example, when employing AZ31 chips as raw materials of the matrix, it has low density of 1.85g/cm<sup>3</sup> and extremely superior mechanical properties, such as tensile strength over 350MPa and Young's modulus of 50GPa, to the conventional Mg-Al-Zn alloys. Concerning to the tribological property under the wet lubricant condition, it shows a low friction coefficient less than 0.04 and no seizure phenomenon with contacting to the S35C steel counter material. In particular, when including the formed MgO particles, the coefficient reduced to 0.02 due to its mild offensive property on the counter part. Its wire and pipe were produced via the mass hot extrusion production in manufacturing plant, and also showed excellent mechanical properties. The optimization of breezing and welding conditions on this developed Mg composite are going in this study.

#### 9:50 AM

**Reaction of Sn-Containing Solders with Nickel Based Under Bump Metallizations:** Guojun Qi<sup>1</sup>; Min He<sup>2</sup>; Zhong Chen<sup>2</sup>; <sup>1</sup>Singapore Institute of Manufacturing Technology, Process Tech. Div., 71 Nanyang Dr. 638075 Singapore; <sup>2</sup>Nanyang Technological University, Sch. of Matls. Eng. 639789 Singapore

This work relates to wafer bumping technology development for flip chip packaging applications in the electronics industry. Nickel is an alternative under bump metallization (UBM) material because of its slower reaction rate with Sn-based solders as compared to Cu-based UBMs. Two types of Ni-based UBMs are widely used: sputtered nickel and electrolessly plated Ni-P alloys (EN). In this study we compared the interfacial morphology of Sn-containing solders (Sn-Ag and eutectic Sn-Pb) with these two types of nickel based under bump metallizations. Both chunky and needle type of intermetallics were observed between the EN UBM and the solders. Their morphology changed with different cooling rates below the melting temperatures of the solders. In the case of the sputtered nickel UBM, there was only a layer of scallop-type intermetallics formed. These differences are discussed in terms of soldering reaction at the interface. Kinetics of the intermetallic growth was also examined on the two UBM systems.

#### 10:15 AM Break

#### 10:35 AM Invited

**Effect of Intense Magnetic Field on CdTe Electro-Deposition:** Toshiyuki Kozuka<sup>1</sup>; Yoshinori Sugita<sup>1</sup>; Masayasu Kawahara<sup>1</sup>; <sup>1</sup>Kumamoto University, Dept. of Matls. Sys., 2-39-1, Kurokami, Kumamoto 860-8555 Japan

CdTe metal composite semi-conducting material has high potential for good performance of energy conversion efficiency, so that there is much room for improvement of energy conversion efficiency according to the processing of making thin CdTe film. In this paper, the imposition of intense magnetic field on CdTe electro-deposition is proposed, which is one of possibility for improving the energy conversion efficiency. In the experiment, cryogen-free superconducting magnet up to 5T was used and CdTe film was deposited electrically in -0.72V vs. SHE. The electrolyte was Cd and Te ammonia alkali solution with controlled temperature in the acrylic cell of 70mm diameter. Intense magnetic field up to 5T can not only make the deposition surface smooth, but also the size of CdTe crystal.

#### 11:05 AM Invited

**Ceramic-Metal Composites Obtained by Reactive Pressureless Counterflow Infiltration/Penetration (RPCI) of a Ceramic Substrate with Two Different Metallic Infiltrants:** V. M. Kevorkijan<sup>1</sup>; <sup>1</sup>Independent Researching, Betnavska cesta 6, Maribor 2000 Slovenia

A new method for faster production of functionally graded metal-ceramic laminates is based on reactive pressureless counterflow infiltration/penetration of a ceramic substrate with two different metallic infiltrants. The porous or dense ceramic preform is pressurelessly infiltrated or penetrated from one side by the first metallic infiltrant to the desired cross section of the preform, producing the top layer made up of the solidified infiltrant and the underlayer consisting of reactive infiltrated preform. The partly infiltrated preform is then completely infiltrated starting from the other side by the second metallic infiltrant, in this way fabricating the internal layer, consisting of the ceramic preform infiltrated with the second infiltrant and the bottom layer formed by the solidified second infiltrant. Systems already investigated include carbide, nitride and boride ceramic performs infiltrated with aluminum and magnesium alloys. The combination of ferrous and non-ferrous infiltrants (aluminum alloys and cast gray iron) was also experimentally studied.

#### 11:35 AM

**Preparation of Vanadium-Doped SnO<sub>2</sub> Nanocrystallites:** Huaming Yang<sup>1</sup>; Weiqin Ao<sup>1</sup>; Chenghuan Wang<sup>1</sup>; Guanzhou Qiu<sup>1</sup>; <sup>1</sup>Central South University, Dept. of Minl. Eng., Changsha 410083 China

The vanadium-doped SnO<sub>2</sub> nanoparticle was synthesized by the co-precipitation reaction and subsequent calcination from the vanadium(III) chloride and tin(IV) chloride. The crystal size, pore size distribution, micrograph and properties of the nanocrystalline powders were examined by differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction (XRD), desorption isotherm (Barrett-Joyner-Halenda method) and transmission electron microscopy(TEM). Thermal treatment of the precipitate powder at 600°C led to the formation of V-SnO<sub>2</sub> nanoparticle of ~10nm in crystal size. Most of the pores in the nanoparticle are about 5-15nm in diameter. Effect of doped vanadium on the crystal size of the nanoparticle was discussed.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing IV

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C5 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday AM      Room: Pacific  
March 5, 2003      Location: San Diego Marriott Hotel

*Session Chairs:* Tsutomu Yamamura, Tohoku University, Sendai, Miyagi Prefecture 980-8579 Japan; Dingfan Qiu, Beijing General Research Institute of Mining and Metallurgy, Wenxing St., Xizhirncai, Beijing 100044 China

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### 8:30 AM Invited

**Extraction and Separation of Metals from Sulfide by Slurry Electrolysis Process (SEP):** *Qiu Dingfan*<sup>1</sup>; Wang Jikun<sup>1</sup>; <sup>1</sup>Beijing General Research Institute of Mining and Metallurgy, Wenxing St., Xizhirncai, Beijing 100044 China

Slurry Electrolysis Process (SEP) is a new hydrometallurgical method and clean technology. Sulfide ores can be treated by SEP without SO<sub>2</sub> emission, and the sulfur from the sulfides will be recovered in element form which is easy to stockpile and can be transported at low cost. In a special slurry electrolysis cell, it can achieve leaching of elements from the feed and electrowinning of metals from the electrolyte at the same time. Because the anode reactions are utilized for leaching some elements, the consumption of the technological energy is decreased. Author has researched the behavior of different metals in the process and point out that separation of metals in some minerals is possible by SEP. Beijing General Research Institute of Mining and Metallurgy (BGRIMM) has researched SEP to treat bismuth concentrate contain S, Be and F from laboratory to pilot-plant and commercial plants. The commercial plant was set up in 1997; it has been in operation since that time. SEP also has advantage of separation some elements. It is especially suitable for treatment of complex concentrates, which could hardly be accepted by any smelter. This kind of mineral contains Pb; Cu, Au, Ag and S. According to the results of lab experiment and pilot-plant test, a new plant to treat complex gold minerals was set up in 1998 and was in operation in 1999.

### 9:05 AM

**Gold Leaching by Using Ammonium Thiosulfate Solution and Gold Recovery by Solvent Extraction and Cementation:** *Toyohisa Fujita*<sup>1</sup>; Liu Kejun<sup>1</sup>; Atsushi Shibayama<sup>1</sup>; Harunobu Arima<sup>2</sup>; Wan-Tai Yen<sup>2</sup>; <sup>1</sup>Akita University, Fac. of Eng. & Resource Sci., 1-1 Tegata Gakuencho, Akita 010-8502 Japan; <sup>2</sup>Queen's University, Dept. of Mining Eng., Kingston, Ontario K7L 3N6 Canada

The effect of variables on the gold extraction with ammonium thiosulfate was investigated on sponge gold and ore samples. The Effects of CuSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, NH<sub>4</sub>OH, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, pH, stirring speed and retention on gold leaching rate and thiosulfate oxidation (consumption) have been studied. Almost 100% of gold was leached from sponge gold and over 96% from ore sample at optimum conditions. Trioctylmethyl ammonium chloride was used to recover gold from thiosulfate pregnant solution. It was found that more than 99% of gold was recovered by the extractant diluted with n-octane at O/A ratio of 1:1 without the re-adjustment of pH or others. Also, the gold cementation was conducted without de-aeration by using zinc, copper and aluminum powders. The result indicated that the gold was effectively recovered from a solution of low ammonia and copper concentrations and higher thiosulfate concentration. The gold recovery process by using ammonium thiosulfate is an environmental friendly method comparing to conventional cyanidation process.

### 9:30 AM

**Corrosion Behaviors of the Pb-Ag-Ca Anodes for Zinc Electrowinning in Sulfuric-Acid Electrolyte:** *Yasushi Takasaki*<sup>1</sup>; Hitoshi Watanabe<sup>1</sup>; Kazuo Koike<sup>1</sup>; <sup>1</sup>Akita University, Fac. of Eng. & Resource Sci., 1-1 Gakuen-cho, Tegata, Akita 010-8502 Japan

In the zinc hydrometallurgical extraction, minimizing of the electric power consumption of the electrowinning process is an important issue for energy saving. At the Zinc & Lead 2000 symposium, the authors suggested that using the Pb-0.5%Ag-0.6%Ca alloy decreased the electrolysis energy compared to the conventional Pb-0.9%Ag alloy. In this study, corrosion behaviors of the Pb-Ag-Ca anodes in sulfuric-acid electrolyte were investigated. Referring to the results for the Pb-0.5%Ag-0.6%Ca anode after 20-days of electrolysis, the bath voltage and the quantity of anode slime were decreased respectively as compared with the Pb-1%Ag anode. Subsequently, beta-PbO<sub>2</sub> was detected by XRD and its peaks were sharper comparing to respective ones of the Pb-1%Ag anode. Moreover, dense beta-PbO<sub>2</sub> layer on the Pb-0.5%Ag-0.6%Ca anode surface was observed. Therefore considering the results, it was suggested that the dense beta-PbO<sub>2</sub> layer of the anode surface was a factor that leads to a lower bath voltage and decreasing quantity of anode slime.

### 9:55 AM

**De-Oiling of Industrial Water Effluents Using Column Flotation:** *F. J. Tavera*<sup>1</sup>; R. Escudero<sup>1</sup>; <sup>1</sup>Universidad Michoacana de San Nicolás de Hidalgo, Inst. de Investigaciones Metalúrgicas, Santiago Tapia 403, Morelia, Michoacán 58000 México

Column flotation technology, at first developed for application in mineral dressing, has received special attention in order to process non-mineral dispersions as a result of its low costs, high efficiency, and relatively simple operation. This paper presents the results from the operation of a laboratory flotation column in order to separate vegetable oil and soap from aqueous industrial effluents. The flotation system was operated under continuous countercurrent conditions, with and without additions of a cationic collector. The experiments have shown that it is possible to separate about 80% of the organic phase in a rougher flotation stage; also, the results in this work suggest that there is an optimum bubble size from which either below or above the recovery of the organic decreases.

### 10:20 AM Break

### 10:30 AM Invited

**Mechanism of the Electrolysis of Rare-Earth Chlorides in Molten Chloride Bath:** *Tsutomu Yamamura*<sup>1</sup>; <sup>1</sup>Tohoku University, Grad. Sch. of Eng., 02 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi Prefecture 980-8579 Japan

Recently, there has been a wide interest in the development of a process for producing rare earths and actinides, and their oxides by a pyro-process using molten salts as operational fluids in nuclear fuel reprocessing. The electrolytic reduction mechanism of rare-earth chlorides such as LaCl<sub>3</sub>, CeCl<sub>3</sub>, NdCl<sub>3</sub>, SmCl<sub>3</sub> and DyCl<sub>3</sub> in alkali chloride baths has been investigated in NaCl, KCl and eutectic LiCl-KCl by means of electrochemical transient methods. The thermodynamic behaviors of rare-earth containing species have been discussed in the frame of Electrode potential - pO<sub>2</sub> diagram. Low current efficiency found in the case of Nd electro-winning has been attributed to the dissolution of Nd into the bath. The analyses of electrochemical measurement required the elucidation of the effects of the factors such as under-potential deposition, metal dissolution, moisture and oxygen.

### 11:05 AM Invited

**The Interfacial Chemistry of Sulfur in the Pressure Leaching of Sulfide Minerals:** *David Dreisinger*<sup>1</sup>; Zhimin Zheng<sup>1</sup>; Jianming Lu<sup>1</sup>; <sup>1</sup>University of British Columbia, Dept. of Metals & Mats. Eng., 309-6350 Stores Rd., Vancouver, BC V6T 1Z4 Canada

The pressure leaching of sulfide minerals has become widely applied for the recovery of base and precious metals. The leaching of zinc sulfide concentrates at 150 °C in the Dynatec Zinc Pressure Leach process has been successfully applied commercially for over 20 years. Pressure oxidation of refractory gold ores containing pyrite and other sulfide minerals has been applied commercially since the 1980's at T > 190 °C. It is widely anticipated that pressure leaching of copper sulfides and in particular chalcopyrite will be the next widespread application of pressure leaching of sulfide minerals. The behaviour of elemental sulfur and the role of surfactants in the pressure leaching of sulfide minerals have received relatively little fundamental study. Sulfur melts at 2119 °C and it is well known that liquid elemental sulfur will tend to wet sulfides and inhibit leaching reactions from proceeding to completion. Surfactants have been widely used in zinc pressure leaching, pressure oxidation of refractory gold ores and are being

advocated for the pressure leaching of chalcopyrite. There are two aspects of the interfacial chemistry of sulfur that have been studied experimentally in a custom built high pressure and high temperature cell. First, the interfacial tension of the liquid sulfur  $\downarrow$ V aqueous solution system has been studied by photographing droplets of liquid sulfur in solution. The shape of the droplets is then used to calculate the interfacial tension. Second, the contact angle between liquid sulfur and various sulfides has been measured in the presence of various aqueous solutions by photographing droplets of liquid sulfur resting on horizontal mineral specimens. All of these measurements have been performed in the absence and presence of surfactants. In this paper, measurements of interfacial tension and contact angles in the liquid sulfur  $\downarrow$ V aqueous solution  $\downarrow$ V mineral system are reported and discussed in relation to current and future applications in zinc, gold and copper pressure leaching.

**11:40 AM**

**Ecologically Safe Technology of Non-Ferrous Metals Obtaining from Sulfide Raw Materials by Means of Bacterial Leaching:** O. V. Slavkina<sup>1</sup>; N. V. Fomchenko<sup>1</sup>; V. V. Biryukov<sup>1</sup>; <sup>1</sup>Moscow State University of Environmental Engineering, 21/4 Staraya Basmannaya St., Moscow 107066 Russia

The principally new two-stage technological realization of bacterial leaching process by means of bacteria *Thiobacillus ferrooxidans* is proposed. Optimal conditions for main electrochemical reactions of sulfides oxidizing must be created for the first stage (the active oxidizing agent supply and reaction products withdrawal). The active concentrate subdivision in two fractions (easy and hard oxidizable) happens here. Then these fractions are to be separated and hard oxidizable fraction is returning to the first stage or can be removed from the process. Easy oxidizable fraction is transferring to the second stage of bio leaching. The first stage duration and the suspension separation procedure are to be calculated according to developed method for every processing concentrate. The second stage of bio-leaching shall be carried-out under high activity of microorganisms. Such conditions are contributing to most complete non-ferrous metals transferring into solution and sulfide sulfur transformation into elemental sulfur with its partial oxidation to sulphate-ion. In addition, the sediment, containing mainly ferric iron, sulphate-ions and hydroxide-ions is forming on the second stage. The quantity of sediment is depending on the processing concentrate and pH at the second stage of bio-leaching process. At the same time the ferric iron equilibrium concentration in solution is determined by these parameters. Ferric iron, being an active oxidizer in bio-solution at optimal pH is returning to the first stage of bio-leaching. Process realization according to proposed technological strategy makes possible to achieve higher rates of bacterial leaching in comparison with traditional one-stage process. At the same time two-stage bio-leaching process is in rather good accordance with standard methods of non-ferrous metals recovery from solutions. It is advisable to organize the stage of non-ferrous metals recovery between the first and the second stage of bacterial leaching. Such way permits to obtain selective sediments of non-ferrous metals while the iron (in the form of the ferrous sulphate) is stayed in the solution.

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## **Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Copper II**

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday AM

March 5, 2003

Room: Santa Rosa

Location: San Diego Marriott Hotel

*Session Chairs:* Florian Kongoli, FLOGEN Technologies Inc., Mats. Tech. Dept., Montreal, Quebec H3S 2C3 Canada; Yasuo Ojima, Sumitomo Metal Mining, Toyo Smelter & Refinery, Saijo, Ehime 793-0005 Japan

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**8:30 AM Keynote**

**Future of Copper Converting Process:** Yasuo Ojima<sup>1</sup>; <sup>1</sup>Sumitomo Metal Mining, Toyo Smelter & Refinery, Otu 145-1 Funaya, Saijo, Ehime 793-0005 Japan

The mainstream of copper smelting process in the world is the combination of Outokumpu type Flash smelting and PS converting process. Presently it will be estimated that in the world copper production about 50% is produced by Flash smelting process and 90% is by PS converting process. PS converting process has been widely used for many smelters more than 100 years owing to its operational flexibility in spite of the batch operation. However, an environmental issue has been pointed out because of the difficulty of fugitive gas handling. Recently several copper smelters in the world have been newly constructed and executed the major modification and modernization. Continuous converting process has emerged some of them instead of PS converting process. This paper describes the comparison of PS and emerging continuous converting process, and the prospect of the future of copper converting process.

**9:00 AM**

**Efficiency of Porous Plugs in Fire Refining of Crude Copper:** C. M. Acuna<sup>1</sup>; M. Sherrington<sup>2</sup>; <sup>1</sup>Codelco, Chuquicamata Div., Chuquicamata Chile; <sup>2</sup>Instituto Nacional de Capacitación, INACAP, Calama Chile

In the fire refining of crude copper the use of porous plugs, by stirring with an inert gas, has been mainly considered as a surface renewing agent to increase product quality and/or shortening the refining cycle. However its application is rather limited, specially because of different industrial practices as well as insufficient data on its aside effects on the refractory lining. Furthermore, the combined stirring-reaction mechanism has to be clarified. The standard procedure in fire refining consist of sulfur removal via air injected through tuyeres, arsenic reduction via soda-lime flux and oxygen control by substoichiometrical air or steam fuel mixtures. In the present study the effect of bottom stirring by use of porous plugs and nitrogen gas injection in the treatment of a dirty crude copper, in the range 400-150 ppm sulfur, approximately 2,500 ppm arsenic and 14,000-9,000 ppm oxygen, was investigated. The combined effect stirring-reducing air/steam: fuel mixtures follows a kinetics of order one where the kinetics constant can be represented by a polynomial of the form:  $K = A * R^2 + B * R + C$  with K as the kinetics constant, A, B and C as constants depending on the stirring nitrogen flow rate and R as the ratio air-fuel or steam-fuel used in the reducing step. If just the oxidation, complexing and reducing steps are considered the process time may be shortened by 30%-40%, depending on the optimization of the air-fuel or steam-fuel mixture used.

**9:25 AM Invited**

**ISASMELT—An Update on Latest Developments:** Philip Arthur<sup>1</sup>; Britt Butler<sup>1</sup>; James Edwards<sup>1</sup>; Chris Fountain<sup>1</sup>; Simon Hunt<sup>1</sup>; Philip Partington<sup>1</sup>; Jorma Tuppurainen<sup>1</sup>; <sup>1</sup>Mount Isa Mines, Ltd., Brisbane, QLD 4000 Australia

The Isasmelt process is making a significant contribution to the global metals industry. Isasmelt furnaces are now operating successfully in eight different countries and treating approximately 3 million tonnes of concentrates and secondary materials per year. The process is currently used in both lead and copper smelting. The most recently commissioned plants were in Germany and China, one for treating scrap copper and the other treating low-quality copper concentrates. The Copper Isasmelt furnace at Mount Isa Mines continues to set new operational records, with throughput of more than 1 million tonnes of concentrate per year and very low operating costs. This paper summarises the latest operational data from the Isasmelt plants and introduces plans for the latest process enhancement, a replacement for Peirce Smith Converters.

#### 9:50 AM

**Development of Sumitomo Premixed Concentrate Burner for Copper Flash Smelting:** *Yasumasa Hattori*<sup>1</sup>; Yoshiaki Mori<sup>1</sup>; Yasuhiro Kondo<sup>1</sup>; Yukihito Sasaki<sup>1</sup>; Toyokazu Okubo<sup>1</sup>; Kozo Baba<sup>1</sup>; <sup>1</sup>Sumitomo Metal Mining Company, Ltd, Niihama Rsrch. Labs., 17-5, Isoura-Cho, Niihama, Ehime 792-0002 Japan

An extensive study including fluid dynamic calculation, cold model tests, pilot plant tests as well as measurements in a concentrate burner of a commercial flash furnace was carried out in order to develop a new Sumitomo flash smelting concentrate burner. The pressure measurements in the commercial burner indicated that the premix of concentrate and reaction air in the burner was insufficient. Pilot plant tests exhibit that the enhancement of the premix of concentrate and reaction air is very effective to improve burner performance. Using the additional pressure drop of the reaction air as an indicator of the premix, a new type Sumitomo premixing concentrate burner was developed.

#### 10:15 AM Break

#### 10:25 AM

**Effect of the Oxygen Potential on the Viscosity of Copper Smelting Slags and its Relation to the Liquidus Surface:** *F. Kongoli*<sup>1</sup>; I. McBow<sup>1</sup>; S. Llubani<sup>1</sup>; <sup>1</sup>FLOGEN Technologies, Inc., Matls. Tech. Dept., 5757 Decelles, Ste. 511, Montreal, Quebec H3S 2C3 Canada

Viscosity is an important parameter of copper smelting and converting processes. It affects the settling of matte or metal droplets in the slag, distribution of elements, etc. Despite this importance, considerable confusion exists on the viscosity of copper smelting slags as a result of many disagreements found among the measured viscosity data of several authors especially in the slags of high ferric iron content and close to magnetite precipitation. In this work the effect of oxygen potential on the viscosity of copper smelting slags has been quantified through a coupled quantification of viscosity and liquidus temperature. The confusion in the literature has been clarified and the importance of the relation between the viscosity and the liquidus temperature is discussed.

#### 10:50 AM Invited

**Two Copper Smelting Processes at Onsan:** *In-Ho Song*<sup>1</sup>; Young-Chul Kang<sup>1</sup>; <sup>1</sup>LG-Nikko Copper, Inc., Daejung-Ri 70, Ulju-Gun, Onsan-Eup, Ulsan City 689-892 Korea

The Onsan flash smelter of LG-Nikko Copper Inc. was commissioned at the capacity of 80,000tpy from copper concentrate in 1979 and its capacity was increased up to 164,000tpy through the two times' expansion in 1988 and 2001. As the Onsan smelter was started Mitsubishi continuous process in 1998, it has two processes within one plant. This paper outlines two processes' difference and operating data, i.e., process flow, feed materials, output product quality, impurity distribution, man power, dust generation ratio, power consumption, productivity, steam production, etc.

#### 11:15 AM

**High-Intensive Operation of Flash Smelting Furnace at Saganoseki Smelter & Refinery:** Masatoshi Ogasawara<sup>1</sup>; *Toshihiro Kamegai*<sup>1</sup>; Masatoshi Maeda<sup>2</sup>; <sup>1</sup>Nippon Mining & Metals Company, Ltd., Saganoseki Smelter & Refinery, Saganoseki-machi, Oita 879-2201 Japan; <sup>2</sup>Metal Economics Research Institute, Japan, Mori Bldg. 11, 2-6-4 Toranomon, Minato-ku, Tokyo Japan

Saganoseki smelter & refinery operated two flash smelting furnaces, producing a combined 330,000 metric tons per year (hereinafter mtpy) of copper. In 1996, however, it successfully shifted to single furnace operation while maintaining production at the same level. Since then, the production capacity has been further increased to the present 450,000 mtpy by technological improvements. Also, in order to reduce the converter load which represents a bottleneck in efforts to increase production, the matte grade was gradually increased and currently runs at 65 to 66% attaining the low slag loss of 0.7 to 0.8%. 27

This paper introduces some improvements, recent operation results and thermodynamic analyses conducted.

#### 11:40 AM

**The Copper Loss in Slag of Flash Smelting Furnace in Tamano Smelter:** *Tsuneo Maruyama*<sup>1</sup>; Nobuyuki Furui<sup>1</sup>; Makoto Hamamoto<sup>1</sup>; <sup>1</sup>Hibi Kyodo Smelting Company, Ltd., No 6-1-1 Hibi, Tamano City, Okayama 706-8511 Japan

In 1972, the Tamano Smelter of Hibi Kyodo Smelting Co., Ltd. went into operation. The Flash Smelting Furnace, used at the Tamano Smelter, was equipped with electrodes that were attached to the settler substitute of the slag cleaning furnace. After that we promoted the development of our own original coke combustion technology. A new Tamano Type Flash Smelting Furnace (T-FSF), without electrodes, was put into operation in 1988. We have continued to improve the technology of coke combustion and combustion the burner. As a result, we have been able to reduce the copper loss in slag as well as achieve stable operation. Furthermore, we have been able to accomplish this while increasing the concentration feed and matte grade. We will continue to strive for high matte grade operation and to raise production efficiency, while paying attention to the important subject of copper loss in slag. In this report, we will present the detailed data with regards to the copper loss in slag reduction, as well as of the influence of the thickness, settling time and coke. We would also like to report the recent operation conditions of the T-FSF.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Alloys Properties

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday PM

Room: Solana

March 5, 2003

Location: San Diego Marriott Hotel

*Session Chairs:* Shigeatsu Nakazawa, Tohoku University, Dept. of Metall., Sendai 980-8579 Japan; Adolf Mikula, Institute of Inorganic Chemistry, Waehringerstrasse 42, Vienna A-1090 Austria

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#### 2:00 PM Keynote

**Zinc-A Possible Component in Lead-Free Solders:** *Adolf Mikula*<sup>1</sup>; <sup>1</sup>Institute of Inorganic Chemistry, Waehringerstrasse 42, Vienna A-1090 Austria

Lead-tin solders are commonly used in electronic packaging due to their unique combination of electrical, chemical, physical, thermal and mechanical properties. Since lead and lead containing alloys cause great environmental concern and health hazards it is necessary to replace lead in solder materials. One of the main driving forces to eliminate lead in solder joints is the fact that the disposal of great amount of electronic equipment in landfills can cause lead to leach out and contain the underground water and subsequently find its way into the human body. Besides environmental concerns also new technological developments require new solders with a variety of improved or new properties. The miniaturisation of electronic devices need smaller and smaller interconnections and a reliable joining must be achieved with smaller volumes of solder materials. In most cases these new materials will be ternary tin or indium alloys. The second element could be Bi, Cu, Ag, and Au and as third elements Zn, Ni, Sb, Al and P must be considered. All these elements have an influence on certain properties. Small amount of zinc will improve in most cases the mechanical properties and the strength of such solders. We investigated the thermodynamic properties and the oxidation behavior of several ternary zinc systems: Al-Sn-Zn, Cu-In-Zn, Ag-Sn-Zn and In-Sn-Zn.

### 2:35 PM

**Activity Measurement of the Constituents in Molten Sn-Ag-In and Sn-Zn-Mg Ternary Lead Free Solder Alloys by Mass Spectrometry:** Takahiro Miki<sup>1</sup>; Naotaka Ogawa<sup>2</sup>; Tetsuya Nagasaka<sup>1</sup>; Mitsutaka Hino<sup>1</sup>; <sup>1</sup>Tohoku University, Dept. of Metall., Grad. Sch. of Eng., Aoba-yama 02, Aoba-ku, Sendai 980-8579 Japan; <sup>2</sup>Tohoku University (Now at NKK Corporation), Sendai 980-8579 Japan

The increase of demand for smaller and lighter portable electronic devices has made interconnecting densities and packaging technologies more important. Soldering material widely used is Sn-Pb alloy, which have low melting point and excellent electrical, strength properties and wettability. However, Pb is one of the toxic elements, which is undesirable due to environmental and safety reasons, thus Pb-free alternative alloy is preferred for new soldering material. Sn-Ag and Sn-Zn based alloys were viewed as very promising candidates, among many potential substitutes. Addition of third element to these alloys will decrease the melting point of the alloy. Hence, Sn-Ag-In and Sn-Zn-Mg alloys are expected to be suitable for replacing Sn-Pb solder alloy. In order to design new Pb-free soldering materials, precise understanding of thermodynamic properties and phase diagrams for alloy systems are crucial. In the present work, ion current ratios of Ag to In and Mg to Zn were measured for Sn-Ag-In and Sn-Zn-Mg alloy by mass spectrometry, respectively. Also, the authors reviewed the thermodynamic properties of terminal binary alloys determined by other researchers and evaluated a thermodynamic function to express the excess Gibbs free energy of each binary alloy. Thermodynamic function to express the excess Gibbs free energy of liquid Sn-Ag-In and Sn-Zn-Mg ternary alloy were determined, utilizing the assessed Gibbs free energy of terminal binary alloys with the measured ion current ratios using mass spectrometer.

### 3:00 PM

**Effect of Additives on Viscosity of Molten Nickel Base Alloys:** Yuzuru Sato<sup>1</sup>; Koji Sugisawa<sup>2</sup>; Daisuke Aoki<sup>2</sup>; Masayoshi Hoshi<sup>2</sup>; Jong-Il Kim<sup>2</sup>; Tsutomu Yamamura<sup>2</sup>; <sup>1</sup>Tohoku University, Dept. of Metall., Aramaki aza Aoba, Sendai 980-8579 Japan; <sup>2</sup>Inha Technical College, Dept. of Metallurg. Eng., Incheon 402-752 Korea

Viscosity has been measured for various binary alloys of nickel with iron, cobalt and chromium to clarify the behavior of viscous flow of molten nickel alloys. Entire concentration range for iron and cobalt, and 0-60at% for chromium were studied. Method for the measurement was an oscillating cup viscometry using an alumina crucible that was precisely machined. Temperature was up to about 1880K for all the measurements. A furnace used was carefully controlled to keep best temperature uniformity that was within 0.5K for entire length of the crucible to prevent the convection in the melt. All the results represented good Arrhenius relationship although some measurements included overcooled temperatures. The isothermal viscosities increased monotonously with an addition of iron and chromium into nickel. On the other hand, the addition of cobalt showed slight decrease, and then viscosity increases in the progress of addition of cobalt.

### 3:25 PM

**Microstructure Analysis of ZA Alloy Rod Directionally Solidified by Heated Mold Continuous Casting:** Ying Ma<sup>1</sup>; Yuan Hao<sup>1</sup>; <sup>1</sup>Gansu University of Technology, Matls. Sci. & Eng., 85 Langongping Rd., Lanzhou, Gansu 730050 China

The as-cast and heat treatment microstructure of ZA alloy rod directionally solidified by continuous casting has been analyzed. The results show that the microstructure of the ZA alloy lines is the parallel directional dendritic columnar crystal. Every dendritic crystal of eutectic alloy ZA5 is composed of many layer eutectic  $\delta$  and  $\zeta$  phase. The microstructure of hyper eutectic ZA alloys is primary dendritic crystal and interdendritic eutectic structure. The primary phase of ZA8 and ZA12 is  $\delta$  phase, but the primary phase of ZA22 and ZA27 is  $\alpha$  phase.

### 3:50 PM Break

### 4:10 PM Invited

**Activities of Bi and In in the Bi-In Liquid Alloy Measured by Using Vacuum-Sealed Quartz Cell/Atomic Absorption Spectrophotometer Combination:** Shigeatsu Nakazawa<sup>1</sup>; Minoru Sunada<sup>2</sup>; Takeshi Azakami<sup>3</sup>; Tetsuya Nagasaka<sup>1</sup>; <sup>1</sup>Tohoku University, Dept. of Metall., Grad. Sch. of Eng., Aoba-yama 02, Sendai 980-8579 Japan; <sup>2</sup>Sunada Kogyo Company, Ltd., Kosugi 406, Tonami 939-1357 Japan; <sup>3</sup>Saitama Institute of Technology, Dept. of Matls. Sci. & Eng., Grad. Sch. of Eng., 1690 Fusaiji, Okabe-machi, Osatogun 369-0293 Japan

Activities of Bi and In in the Bi-In liquid alloy were measured over the whole range of composition at the temperature from 850K to 1050K. An alloy was vacuum-sealed in a quartz cell and heated at the temperature of interest. The absorption for 307nm radiation from Bi lamp was measured for Bi atom vapor in the cell. By heating a pure

metal as a standard and measuring the absorbance as a function of the temperature, an analytical curve for Bi atom vapor was constructed and used for conversion of the absorbance to the vapor density. Bi activity was determined as the ratio of the Bi atom vapor density over the alloy to that over a pure metal. The same procedure was applied to In vapor and In activity was determined independently of Bi. Results were used to reevaluate the thermodynamics of the Bi-In system.

### 4:40 PM

**Thermodynamic Properties of Several Ternary Zinc Alloys:** Adolf Mikula<sup>1</sup>; Sabine Knott<sup>1</sup>; <sup>1</sup>University of Vienna, Inst. für Anorganische Chemie, Währingerstrasse 42, Vienna A-1090 Austria

In this presentation I would like to show the importance of good, reliable and consistent thermodynamic data for industry and for research. The thermodynamic properties of several ternary liquid zinc alloys were determined using emf and calorimetric measurements. The Au-Sn-Zn, Ag-Sn-Zn, Cu-In-Zn and Al-Sn-Zn alloys were investigated because they are possible candidates for new lead-free solder materials. In these systems the thermodynamic data can be used to improve phase diagram calculations and will be helpful for some theoretical models to improve the calculation of physical or mechanical properties. In the Au-Sb-Zn, Ag-Sb-Zn and Cu-Sb-Zn the temperature dependence of the thermodynamic data was used to look for the existence of Chemical Short Range Order (CSRO) in the melt of these alloys.

### 5:05 PM

**Defect Formation and Mechanism of ZA Alloy Made in Continuous Casting by Heated Mold:** Ying Ma<sup>1</sup>; Feng-yun Yan<sup>1</sup>; Hong-jun Liu<sup>2</sup>; <sup>1</sup>Gansu University of Technology, Sch. of Matls. Sci. & Eng., Lanzhou 730050 China; <sup>2</sup>Huazhong University of Science and Technology, Sch. of Matls. Sci. & Eng., Wuhan 430074 China

The continuous directional solidification technique of five kinds of special ZA alloys with eutectic, peritectic and eutectoid transformation under the condition of continuous casting by heated mold was studied. The mechanism of surface defects appearing in ZA alloy line was discussed and the structure of some defects were analyzed by SEM. The results show that only when the fitting of various technique factors, pressure head, outlet temperature, pulling speed and cooling condition is reasonable under a certain range, can the ZA alloy smooth line be continuously pulled out. Unreasonable technique will result in hot tear, rough surface, mush outlet, leaking and other defects. The shape and location of solid-liquid zone have the importance influence on the forming of above defects. When the solid-liquid zone is located in the mould outlet or inner mould, the surface of solidification will protrude into the inner mould. If the left liquid cannot counteract the solidification contract, the rough surface will appear. If the solidification surface further into the mould, the ingot in mould will have a big friction force when pulling and form hot tear. When the solid-liquid zone is moved out of mould, the solidification surface will turn into a plane, which made it easy to form leaking. The vibration or unstable operation will make the ingot winding during pulling.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Materials Processing Technologies: General II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday PM                      Room: Point Loma  
March 5, 2003                        Location: San Diego Marriott Hotel

*Session Chair:* Thomas P. Battle, Dupont, Edge Moor, DE 19809 USA

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### 2:00 PM Invited

**Development of Closed Recycling Process for Low Grade Scrap of Al-Based Composite Materials:** *Hiroyuki Sano*<sup>1</sup>; Shinichi Kato<sup>2</sup>; Tatsuya Motomura<sup>2</sup>; Toshihuru Fujisawa<sup>1</sup>; <sup>1</sup>Nagoya University, Rsrch. Ctr. for Adv. Waste & Emission Mgt., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan; <sup>2</sup>Nagoya University, Dept. of Matls. Sci. & Eng., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

Closed recycling process for low grade scrap of Al-based composite materials was developed. Flux treatment with water soluble halide is a key technique in this process. In the present work, flux treatment conditions were discussed from the viewpoint of separation and recovery of matrix, reinforce and flux materials. Optimum separation condition was obtained for the NaCl-KCl-KF flux treatment. Recovered aluminum alloy has enough quality for using various materials. Used flux is recyclable for the process by adding a small amount of KF.

### 2:35 PM

**Two-Way Shape Memory Effect of Ferromagnetic Ni-Mn-Ga Sputter-Deposited Films:** *Makoto Ohtsuka*<sup>1</sup>; Minoru Matsumoto<sup>1</sup>; Kimio Itagaki<sup>1</sup>; <sup>1</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., 2-1-1, Katahira, Aoba-ku, Sendai 980-8577 Japan

The ternary intermetallic compound Ni<sub>2</sub>MnGa is an intelligent material, which has a shape memory effect (SME) and a ferromagnetic property. Use of shape memory alloy films for an actuator of micro-machines is very attractive because of its large recovery force. The Ni-Mn-Ga films with a thickness of nearly 5 μm were deposited with a radio-frequency magnetron sputtering apparatus. They were heat-treated at 1073 K for 36 ks for homogenization and ordering. The purpose of the present study is to investigate the effects of fabrication conditions on the properties of the films such as chemical composition, crystal structure, microstructure and transformation temperature. Furthermore the effect of plastic deformation and of constraint aging on SME is also investigated. The two-way SME was shown after plastic deformation. The intensity of X-ray diffraction peaks from stress-induced martensitic phase was found. The constraint-aged films also showed the two-way SME by thermal cycling.

### 3:00 PM

**Fabrication of BaNd2Ti4O12/Bi4Ti3O12/BaNd2Ti4O12 Laminated Ceramics by Spark Plasma Sintering:** *Yong Jun Wu*<sup>1</sup>; Naofumi Uekawa<sup>1</sup>; Kazuyuki Kakegawa<sup>1</sup>; <sup>1</sup>Chiba University, Ctr. for Frontier Elect. & Photonics, Dept. of Matl. Tech., Chiba 263-8522 Japan

Laminated ceramics have received wide scientific and commercial attention because its properties, such as mechanical properties and electrical properties, can be tailored by adjusting the structure, thickness and composition of the different layers. For example, ferroelectric Bi4Ti3O12 (BIT) which has a positive temperature coefficient of dielectric constant (te) can be used to modify the negative te of typical microwave dielectric ceramic BaNd2Ti4O12 (BNT). However, BaNd2Ti4O12/Bi4Ti3O12/BaNd2Ti4O12 (BNT/BIT/BNT) laminated ceramics could not be prepared by the general method because the optimal sintering temperature of BaNd2Ti4O12 ceramic (around 1350°C) was much higher than that of Bi4Ti3O12 ceramic (around 1100°C). In this research, a new method of spark plasma sintering (SPS) combined with post-sintering was successfully proposed to prepare BNT/BIT/BNT laminated ceramics. It was divided into three steps. In first step, the BaNd2Ti4O12 ceramics were prepared by conventional sintering method. In second step, the calcined and pre-pressed Bi4Ti3O12 powders were sandwiched between BaNd2Ti4O12 ceramic pellets and spark plasma sintered at 900°C for 10min to synthesize BNT/BIT/BNT composite ceramics. In last step, a post-sintering was employed to re-oxidize the partially reduced BNT/BIT/BNT composite ceramics. The results of scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) showed that BNT layer and BIT layer were well bonded and no significant interfacial infiltration between them was observed. The sandwiched BNT/BIT/BNT ceramic with 10.7% BIT in volume has a dielectric constant of 92.8, a low dielectric loss of 0.0068 and a small temperature coefficient of dielectric constant of 35 ppm/°C at 1 MHz.

### 3:25 PM

**Preparation of Infrared Materials from Ultrafine Quartz Powder:** *Huaming Yang*<sup>1</sup>; Jianhong Chao<sup>1</sup>; Weiqin Ao<sup>1</sup>; Guanzhou Qiu<sup>1</sup>; <sup>1</sup>Central South University, Dept. of Minl. Eng., Changsha 410083 China

Infrared material is a special material widely used in military, biological engineering and chemical industry, but the problems, such as unstable property, high cost and higher thermal expansion coefficient, seriously restrict the development and wide application of traditional infrared materials with SiC or ZrSiO4 matrix. Ultrafine quartz powder was used to prepare infrared material by Hot-pressing technology. The aim of the paper is to investigate the thermal expansivity and effects of

SiO2 size, addition of Al2O3 or Fe2O3 on infrared emissivity of quartz matrix infrared material(QMIM) in 8-25μm wavelength range. The results indicate that 89% of infrared emissivity and 0.4×10<sup>-5</sup>/°C of thermal expansion coefficient of QMIM can be obtained. Affecting mechanism of Al2O3 and Fe2O3 on infrared emissivity of QMIM were also discussed.

### 3:50 PM Break

### 4:10 PM

**Deposition of Multilayered Titanium Thin Film by Nd: YAG Laser Ablation:** *Takahiro Nakamura*<sup>1</sup>; Hideyuki Takahashi<sup>2</sup>; Katsutoshi Yamamoto<sup>3</sup>; Nobuaki Sato<sup>3</sup>; Atsushi Muramatsu<sup>3</sup>; Eiichiro Matsubara<sup>2</sup>; <sup>1</sup>Tohoku University, Dept. of Matl. Sci., Katahira 2-1-1, Aoba-ku, Sendai 980-8577 Japan; <sup>2</sup>Tohoku University, Inst. for Matl. Rsrch., Katahira 2-1-1, Aobaku, Sendai 980-8577 Japan; <sup>3</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls., Katahira 2-1-1, Aobaku, Sendai 980-8577 Japan

The thin film of TiO2 by means of laser ablation has the nano-structure and would appear the new properties. Multilayered TiO2/Ti thin film on quartz substrate was synthesized by laser ablation of Ti and TiO2 targets using Nd: YAG pulse laser under the established conditions. Namely, Ti and TiO2 film was successively deposited on the substrates by the irradiation using laser light of the energy 500 and 400 mJ and the repetition rate 50 Hz for 15 and 6 sec with Ti and TiO2 target, respectively, in a high vacuum reaction chamber under the oxygen pressure of 10-8 Torr. Thicknesses of Ti and TiO2 in as-prepared film are 150 and 210 nm with growth rates of about 10 and 35 nm/sec, respectively. Preparation of TiS2/TiO2/Ti multilayered film was also examined in the presence of oxygen and H2S (or CS2) with Ti and/or TiO2 target.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Aqueous and Electrochemical Processing V

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPM/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday PM

Room: Pacific

March 5, 2003

Location: San Diego Marriott Hotel

*Session Chairs:* Paulo von Krüger, Federal University of Ouro Preto, Minas Gerais Brazil; U. B. Pal, Boston University, Dept. of Mfg. Eng., Boston, MA 02446 USA

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### 2:00 PM Invited

**Zirconia-Based Inert Anodes for Green Synthesis of Metals and Alloys:** C. P. Manning<sup>1</sup>; A. Krishnan<sup>1</sup>; U. B. Pal<sup>1</sup>; <sup>1</sup>Boston University, Dept. of Mfg. Eng., Boston, MA 02446 USA

The research work demonstrates the technical viability of employing zirconia-based inert anodes for environmentally sound and cost-effective production of metals such as magnesium, tantalum, aluminum, etc., directly from their oxides. The inert anode consists of the oxygen-ion-conducting stabilized zirconia membrane in intimate contact on one side with a catalytically active electronic phase. The opposite (other) side of the zirconia membrane is placed in contact with an ionically conducting solvent phase containing the oxides of the desired metals. An inert cathode is placed in the solvent and an appropriate electric potential is applied between the electrodes to synthesize the metals from their oxides in the solvent. The full-benefit of the process can be realized if it is conducted at temperatures between 1200-1400°C. At these temperatures the ohmic resistance drop across the stabilized zirconia membrane are low and therefore high current densities on the order of 1 A/cm<sup>2</sup> or greater can be obtained. In addition, the process efficiency can be further increased by directly reforming hydrocar-

bon fuel over the anode. It should be noted that several attempts have been made earlier to employ this concept at temperatures below 1000°C. However, these efforts have not been successful mainly because sufficiently high current densities could not be obtained through the zirconia membrane. This paper reports the recent progress of a continuing laboratory-scale investigation involving different types of zirconia-based inert anodes employed at temperatures between 1200-1400°C. The topics covered include: stability of the zirconia membrane in the selected molten solvent (flux), volatility of the flux, potentiodynamic sweeps, electrolysis experiments, and analysis of the metals produced.

### 2:35 PM Invited

**Hydrometallurgical Process for Recycle of Spent Nickel-Metal Hydride Secondary Battery:** *Toshihiro Kuzuya*<sup>1</sup>; Takayuki Naitou<sup>2</sup>; Hiroyuki Sano<sup>1</sup>; Toshiharu Fujisawa<sup>1</sup>; <sup>1</sup>Nagoya University, Rsrch. Ctr. for Adv. Waste & Emission Mgmt., Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan; <sup>2</sup>Nagoya University, Dept. of Matls. Sci. & Eng., Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan

A hydrometallurgical process has been developed for recovery of metal values such as Co, Ni and rare earths from the electrode materials of spent nickel metal-hydride(Ni-MH) secondary battery. MmNi5 intermetallic compound could be separated from the electrode materials mixture by sedimentation. A typical chemical composition of MmNi5 was approximately, in mass%, 56.0%Ni, 13.4%Ce, 10.6%La and 7.9%Co. The time dependency of leaching intermetallic compound with sulfuric acid solution was examined with processing factors such as sulfuric acid concentration, temperature and agitation intensity. The leaching of rare earth metals proceeded very rapidly, reaching completion in less than 1.8ks. On the other hand, the slow leaching of nickel was observed. The percent of nickel leached at 328K could only reach about 70%.

### 3:05 PM

**Rare Earth Separation and Recycling Process Using Rare Earth Chloride:** *Testsuya Uda*<sup>1</sup>; Masahiro Hirasawa<sup>2</sup>; <sup>1</sup>California Institute of Technology, Matls. Sci., MC138-78, Pasadena, CA 91125 USA; <sup>2</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls. (IMRAM), 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan

We review our recent achievements of rare earth separation technique and new process idea for rare earth magnet recycling. (1) Binary chloride mixtures of rare earths were separated by new selective reduction-vacuum distillation process. According to our experimental results, apparent separation factors were 8.1 for Pr-Nd chloride mixture and 570 for Nd-Sm chloride mixture. These values are higher than conventional solvent extraction methods. (2) A study of recycling process of magnet sludge was carried out. The rare earths in the neodymium magnet sludge were extracted by chlorination with FeCl<sub>2</sub>. An activated carbon was used as a de-oxidation reagent. Metallic iron in the sludge was not chlorinated because the iron monochloride is not stable. The extracted rare earth chlorides were easily separated from Fe-alloy and the excess of FeCl<sub>2</sub> by vacuum distillation. 96% of neodymium and 94% of dysprosium in the sludge were extracted into chloride phase. By the vacuum distillation, a mixture of neodymium and dysprosium trichlorides of 99.2% purity was recovered. It was confirmed that the rare earth chlorides were converted to the corresponding oxides by a pyrohydrolysis reaction accompanied by gaseous HCl formation. The HCl gas can chlorinate metallic iron to FeCl<sub>2</sub>. Therefore, a new recycling process for rare earth magnet waste can be realized as a chlorine circulation type process. During the process, only carbon and water are consumed, and there are no toxic pollutants. Moreover, the obtained rare earth oxide can be directly used as raw material in the conventional oxide electrolysis process.

### 3:30 PM

**A Novel Application of Electrorefining in a Membrane Cell to Reclaim Zinc from the Bottom Dross of Hot Dip Galvanization:** *Levente Becze*<sup>1</sup>; Tamás I. Török<sup>1</sup>; <sup>1</sup>University of Miskolc, Dept. of Nonferrous Metall., Miskolc-Egyetemvaros, Miskolc 3515 Hungary

The zinc bottom dross is obtained as a by-product from hot dip galvanizing operations and contains at least 92% zinc, which is recycled mainly by pyrometallurgical processes. The overall costs of such a treatment, however, are often relatively high, and the very strict environmental protection regulations might also cause additional difficulties for the high temperature procedures in the future. Therefore, a novel hydro-elektrometallurgical process has been developed in our laboratory, which could reclaim zinc of high purity, while attempting to achieve low energy consumption and making allowances for all the environmental restrictions. This aqueous processing technique, based on electrolytic refining in a cell equipped with anion-exchange membrane to separate the anode and cathode compartments, allows the indirect purification of the anolyte. Zinc is dissolved from the anode

along with some of the impurity elements, while the intermetallic compounds (Fe-Zn, Fe-Al-Zn) are accumulated in the anode slime.

### 3:55 PM Break

### 4:05 PM Invited

**Fundamental and Applied Research on Tin Electrorefining, Employing Stainless Steel Cathodes:** *Paulo von Krüger*<sup>1</sup>; Erivelto Luis de Souza<sup>2</sup>; <sup>1</sup>Federal University of Ouro Preto, Dept. of Met. Eng., Sch. of Mines, Minas Gerais Brazil; <sup>2</sup>Fundação Gorceix, Ouro Preto, Minas Gerais Brazil

This paper deals with the cell design and operation of a tin electrorefining 1:5 pilot plant. The purpose was the fitting of the basic parameters to be used in a full scale tankhouse, for a major Brazilian tin producer. The main difference was the use of permanent, stainless steel cathodes, instead of the conventional tin starting sheets. The results on both product quality and operating parameters are discussed.

### 4:40 PM

**Separation of Elements in Stainless Steel by Electrorefining Process:** *Toshihide Takenaka*<sup>1</sup>; Masahiro Kawakami<sup>1</sup>; Masao Kawaguchi<sup>1</sup>; <sup>1</sup>Toyohashi University of Technology, Dept. of Production Sys. Eng., Hibarigaoka 1-1, Tempaku-cho, Toyohashi, Aichi-Prefecture 441-8580 Japan

Stainless steel is one of the major materials in a nuclear reactor. The management of radioactivated stainless steel will become an important subject in the near future. The half-life of radioactive elements of Fe and Cr are short in general, whereas those of Ni is very long. Therefore, the separation of the elements in stainless steel should be effective to reduce the management cost of the waste radioactivated stainless steel. In this study, the separation of the elements in stainless steel was investigated by an electrorefining technique in an aqueous solution. The electrochemical reactions of the elements in stainless steel were studied by voltammetry, and potentiostatic electrolysis was carried out. A plate of austenitic stainless steel, SUS304, was used as an anode and a cathode. The anode was dissolved electrochemically with good anodic current efficiency in a chloride solution, while the anodic dissolution did not occur in a sulfate solution. The smaller the anodic overpotential was, the lower the Ni concentration in the solution was after electrolysis. The residue where Ni was concentrated was found on the anode. At the cathode, metallic electrodeposit was obtained by potentiostatic electrolysis, and only a small amount of H<sub>2</sub> gas was evolved simultaneously. The electrodeposit at the cathode consisted of Fe and Cr mainly, and the Ni content was less than 0.5wt% under the suitable condition. It is concluded that the electrorefining technique in a chloride solution can be applied for separation of the elements of stainless steel.

### 5:05 PM

**Preparation of Fibrous Nickel Oxide Powder by Wet Chemical Precipitation Combined with Pyrolysis:** *Zhang Chuanfu*<sup>1</sup>; Jing Zhan<sup>1</sup>; Xueyi Guo<sup>1</sup>; Masazumi Okido<sup>2</sup>; <sup>1</sup>Central South University, Col. of Metallurg. Sci. & Eng., Yuelu Dist., Changsha, Hunan 410083 China; <sup>2</sup>Nagoya University, Ctr. Integrated Rsrch. in Sci. & Eng., Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

In this study, the process of wet chemical precipitation of nickel ions from the solution with oxalic acid followed with precursor pyrolysis has been employed to prepare the fibrous NiO powder. The influences of the pH value, reaction temperature, concentrations of reactants, the order of reagents adding and the addition of surfactant on the morphology of precursor were investigated for the wet chemical precipitation stage; and that of the morphology of precursor, temperature and time for decomposition, air flow, and the rate for heating on the morphology, particle size and specific surface area of the final obtained NiO particles during pyrolysis were addressed respectively. The results show that the fibrous NiO particles with 100-120 for axis-ratios and about 6.0 m<sup>2</sup>/g for specific surface area can be obtained under certain experimental conditions. Spherical nanometer NiO powder particles were obtained after further grinding of fibrous nickel oxide particles.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Copper III

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday PM      Room: Santa Rosa  
March 5, 2003      Location: San Diego Marriott Hotel

*Session Chairs:* Lauri Holappa, Helsinki University of Technology, Lab. of Metall. FIN-02015 HUT Finland; Motoo Goto, Port Kembla Copper Pty. Ltd., Port Kembla, NSW 2505 Australia

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### 2:00 PM

**Effect of Oxygen Enrichment on the El Teniente Converter Productivity at Ilo Smelter, Perú:** *Jose Bengoa*<sup>1</sup>; Jose Palacios<sup>2</sup>; Mario Sanchez<sup>3</sup>; <sup>1</sup>Southern Peru Copper Company, Ilo Smelter, PO Box 35, Ilo Peru; <sup>2</sup>University of Atacama, Dept. Met. Eng., PO Box 240, Copiapo Chile; <sup>3</sup>University of Concepcion, Dept. Met. Eng., PO Box 53-C, Concepción Chile

Low metal prices and environmental restrictions are always a challenge for copper smelters operation and its productivity. Thus, in order to reduce production costs and control gas emissions, improvements of El Teniente Converter operation were made at Ilo Smelter Plant of Southern Peru Copper Co., Ilo, Peru, and the main objective was to increase its capacity for smelting copper concentrates without affecting normal operation. The present work corresponds to a recent study conducted during the normal industrial operation of El Teniente Converter in this plant and, it shows the effect of increasing air oxygen enrichment from 28 to 34% on its productivity. The results show an increasing of concentrate smelting rate from 800 to 1370 tpd and hence a notorious improving in copper production, and practically no effect on the refractory consumption. Additionally, the increment of the concentrate throughput increases SO<sub>2</sub> concentration in the exhausting gas and the sulfuric acid production, showing the effort done by this operation in order to accomplish the environmental Peruvian regulation.

### 2:30 PM

**Oxidation of Copper at Different Temperatures:** *Gabriel Plascencia*<sup>1</sup>; Torstein Utigard<sup>1</sup>; <sup>1</sup>University of Toronto, Matls. Sci. & Eng., 184 College St., Toronto, Ontario M5S 3E4 Canada

Copper was oxidized in the temperature range from 300 to 1000°C under different partial pressures of oxygen. In the range from 300 to 500°C, copper oxidizes following the logarithmic rate law; while in the range from 600 to 1000°C copper oxidizes following the parabolic rate law. Transition from logarithmic to parabolic growth occurs at 525°C. X-ray diffraction was performed on oxide scale to account for the CuO/Cu<sub>2</sub>O ratio at different temperatures. Activation energies found in this work are in good agreement with those already reported.

### 2:55 PM

**YCC ISASMELT Project—The First Chinese ISASMELT Furnace:** *Yun Li*<sup>1</sup>; Philip Arthur<sup>2</sup>; <sup>1</sup>Yunnan Copper Corporation, Wangjiaqiao, Western Hill Dist., Kunming, Yunnan 650102 China; <sup>2</sup>MIM Process Technologies, ISASMELT, Level 2, 87 Wickham Terrace, Brisbane, QLD 4000 Australia

In 1999 Yunnan Copper Corporation made a decision to carry out technical modification on the copper smelter and change the existing sinter plant/electric furnace process to ISASMELT/electric furnace slag cleaning. The ISASMELT furnace has been running smoothly since heatup in May 2002. The design capacity for the ISASMELT furnace is 600,000 tonnes of dry copper concentrate per year. The main aim of the project was to improve environmental performance and decrease energy consumption. Generally the project is going

smoothly at the current stage, due to selection of reliable and successful technology. Good preparation work was done. The extensive training program for key people in Mount Isa Copper Smelter improved the technical people's understanding of the process greatly and ensured successful hand-over of the process technology. The paper describes the plant layout and initial operating data.

### 3:20 PM

**Modelling of Chalcocite Concentrate Flash Smelting:** *Zdzislaw Mieczkowski*<sup>1</sup>; Jozef Czernecki<sup>1</sup>; Zbigniew Smieszek<sup>1</sup>; <sup>1</sup>Institute of Non-Ferrous Metals, Sowińskiego 5, Gliwice 44-100 Poland

KGHM Polska Miedz S.A. applied single-stage process for copper production from chalcocite concentrates in flash furnace. The paper contains model of complex oxidation process of single concentrate grain smelted at KGHM. Description takes into consideration main chemical reactions, heat and mass transfer phenomena, inside the grain as well as between the grain and gas environment. Two zones of process course inside the grain were distinguished. The first zone moves faster within the grain and is caused by increase of temperature inside. Liberation of carbonate and organic carbon occurs there. Second zone penetrates the grain at lower rate. The rate is determined by oxygen presence. Second zone is the place where sulphur is eliminated and vapours of organic compounds are oxidised. On the basis of lab tests results, coefficients characterising oxygen transfer within the grain and determining the rate of chemical reactions were calculated. Model calculations results for single concentrate grain processed in the environment of various oxygen content and model calculations results for concentrate flux smelted in the lab reactor system are presented.

### 3:45 PM Break

### 3:55 PM Invited

**Copper Converting Versus Steel Converting—A Critical Comparison:** *Lauri Holappa*<sup>1</sup>; Heikki Jalkanen<sup>1</sup>; <sup>1</sup>Helsinki University of Technology, Lab. of Metall., PO Box 6200, Hut 02015 Finland

Copper converting is mostly performed in Peirce-Smith converters. The process is still very similar to the original one from the late 19th century: a batch process in a horizontal cylindrical reactor with air blowing via tuyeres along the length of the reactor side. This converter is sometimes called Bessemer converter as Bessemer proposed a similar converter to steelmaking. However, finally he came to a vertical pear-shaped converter with air bottom-blowing. In steel converting, a clear continuum can be perceived from air-blowing Bessemer & Thomas processes to oxygen converter processes (LD or BOP) using top-blowing via a lance, to oxygen bottom-blown converters (OBM or Q-BOP) with special tuyeres, and finally to nowadays combined blowing converters utilizing the advances of both top and bottom blowing. In copper converting similar ideas were missing or at least did not lead to large scale success, with the exception of top-blown rotary converters (TBRC or Kaldo) which were used in small extent both for steel and non-ferrous converting. On one respect copper converting has taken a leading position i.e. in the progress of continuous converting. Mitsubishi process as well some new processes like Ausmelt make continuous converting of matte to blister copper by oxygen-air blowing via top lances. A different principle for continuous converting is flash converting by Kennecott-Outokumpu which fully utilizes the exothermic reactions in smelting and converting solid fine matte particles in a reactor shaft similar to Outokumpu matte flash smelting. Although numerous ideas and principles have been tested for continuous steelmaking it seems to be still far from commercial breakthrough. The paper discusses principal physico-chemical and process technical similarities and differences in copper and steel converting. The main processes are reviewed and compared, and the trends are discussed in respect of eventual exchange of knowledge between ferrous and non-ferrous metallurgy.

### 4:20 PM

**Effect of Electric and Magnetic Fields on Metallic Inclusions in a Liquid Slag:** *Andrzej Warczok*<sup>1</sup>; *Gabriel Riveros*<sup>1</sup>; <sup>1</sup>Universidad de Chile, Av. Tupper 2069, Santiago 2777 Chile

Liquid slags produced in smelting of copper concentrates contain copper in a dissolved form as well as mechanically entrained inclusions of copper matte. Coalescence and sedimentation of inclusions during slag cleaning plays a key role in copper recovery. Liquid matte inclusion in a molten slag presents a system of metallic conductor in an ionic solution. Constant electric field induces migration of the matte droplet along current lines. Additional phenomena occur in a system under crossed electric and magnetic fields. Electromagnetic buoyancy force acting on the inclusion affects its settling rate. Electromagnetic buoyancy force of insulating and metal spheres has been measured in a liquid synthetic slag. It was found that depolarisation of metal sphere, related to the electrode reactions occurring at the surface, plays an

important role in determination of direction and magnitude of the electromagnetic force. On the basis of existing theories and results of measurements the mathematical model, describing the behaviour of metallic inclusions in the liquid slag under the influence of crossed electric and magnetic fields, was developed. Simulation of behaviour of copper matte inclusions under crossed fields showed trajectory of motion in a liquid slag as a function of the slag properties and the inclusion size.

4:45 PM

**Factors Affecting the Rate of Copper Reduction During Copper Refining:** *Gabriel Riveros*<sup>1</sup>; Andrzej Warczok<sup>1</sup>; Leandro Voisin<sup>1</sup>; Tanai Marin<sup>1</sup>; <sup>1</sup>Universidad de Chile, Av. Tupper 2069, Santiago 2777 Chile

Fire refining of copper consists of two stages oxidation and reduction of copper. Very frequent the capacity of anode furnace is determined by the rate of copper reduction. Analysis of factors affecting the rate of oxygen reduction from a liquid copper with solid carbon or injected hydrocarbons pointed out the role of mass transfer in a liquid copper in final stage of reduction. Experimental results of copper reduction with graphite and injected natural gas in a crucible scale showed two stages of the reduction process with a sharp change of controlling mechanism. Estimated dynamic surface area of gas bubbles based on measured bubble frequency and gas flowrate allowed for determination of reaction constant as a function of gas injection intensity and degree of partial pre-combustion of air/natural gas mix. The variation of reductant utilisation as a function of oxygen concentration and temperature has been evaluated based on the determined kinetic model. Possibilities of intensification of copper reduction in fire refining has been discussed on the basis of obtained kinetic data and analysis of various factors determining the time of reduction.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Iron and Steel Making Fundamentals II

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Wednesday PM  
March 5, 2003

Room: Leucadia  
Location: San Diego Marriott Hotel

*Session Chairs:* Fumitaka Tsukihashi, The University of Tokyo, Dept. of Adv. Mats. Sci. Grad. Sch. of Frontier Scis., Tokyo 113-8656 Japan; Mitsutaka Hino, Tohoku University, Dept. of Metall. Grad. Sch. of Eng., Sendai 980-8577 Japan

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2:00 PM Invited

**Simulation on the Formation, Dripping and Penetration Behavior of Primary Oxide Melt in the Pyrometallurgical Process:** *Mitsutaka Hino*<sup>1</sup>; Atsushi Kumano<sup>1</sup>; Kenko Shimizuno<sup>2</sup>; Tetsuya Nagasaka<sup>1</sup>; <sup>1</sup>Tohoku University, Dept. of Metall., Grad. Sch. of Eng., Sendai 980-8579 Japan; <sup>2</sup>Fujitsu Company, Kawasaki Japan

Primary melt, which appears in the ore during heating, plays an important role in many pyrometallurgical processes. For example,  $Al_2O_3$  is known to be enriched in the primary melt which is formed in the lower part of the ironmaking blast furnace, so that such primary melt could possibly penetrate into micro-porosity of sinter ore and result in the harmful effect on the reducibility of the ore. With keeping such background in view, it has been observed the dripping behavior of  $Fe_1O-CaO-SiO_2-Al_2O_3-MgO$  slag from the iron funnel, which has simulated the micro-porosity of sinter ore with the wide range of basicity,  $Al_2O_3$ ,  $Fe_1O$  and  $MgO$  contents. The effect of  $MgO$  on slag dripping behavior has been summarized in this paper. Premelted slag sample was charged on the iron funnel, suspended in the furnace from thermobalance and heated under Ar stream at 4K/min. Dripping of melt from the funnel and slag hold-up were detected by weight change and its temperature was measured. It was found that the hold-up of the

$MgO$  free slag increased with increasing  $Al_2O_3$  content, while this trend became weaker with increasing of the basicity. The addition of 2mass%  $MgO$  resulted in large increase of hold-up on the most of the conditions. When  $Fe_1O$  content was less than 20mass% and the basicity was lower than 0.8,  $MgO$  lowered the hold-up even if the slag contained 10mass%  $Al_2O_3$ . Every slag hold-up showed the minimum at the basicity of less than unity. This trend became remarkable when the slag contained 2mass%  $MgO$ .

2:30 PM Invited

**New Reactor Concepts for Direct Coal-Based Continuous Steelmaking:** *Noel A. Warner*<sup>1</sup>; <sup>1</sup>The University of Birmingham, Cheml. Eng., Edgbaston, Birmingham B15 2TT UK

Modern steelmaking is based on direct use of oxygen in high intensity batch reactors. A totally new approach is proposed in this paper, based on the view that pursuit of high intensity is unlikely to lead to successful coal-based continuous steelmaking. By substituting carbon dioxide and water vapor as the oxidants rather than using oxygen directly, the intensity is greatly reduced. Accordingly, subsurface formation of carbon monoxide bubbles can be avoided by careful manipulation of the three participating rate processes, gaseous diffusion, interfacial chemical kinetics and liquid phase mass transfer. Steelmaking can then be carried out without explosive ejection of molten droplets and the generation of micro-spray but rather in a controlled and fumeless fashion. The vital component is the introduction of generic melt circulation technology. Three melt circulation loops in series are envisaged. Starting with a composite feed of iron ore fines, pulverized coal and lime flux, a metallized solid raft floating on molten iron is propelled out of the ironmaking loop onto the first of two downstream steelmaking loops. In the first, a liquid slag is formed, primary decarburization is undertaken not with oxygen but rather with  $CO_2$  and  $H_2O$  and the melt is desulfurized. The semi-product stream enters the third melt circulation loop, where open-channel decarburization is effected along with dephosphorization to yield a low carbon steel product. Alternatively, the melt leaves the last loop to irrigate a packed tower countercurrent to argon at around 100 mbar to continuously produce ultra-low carbon (ULC) steel.

2:55 PM

**Kinetics and Morphological Studies of a Carbon Composite Briquette Aiming the Emergent Ironmaking Technologies:** *José Carlos D'Abreu*<sup>1</sup>; José Henrique Noldin<sup>2</sup>; Karla de Melo Martins<sup>1</sup>; <sup>1</sup>Catholic University, DCMM, Rua Marques de São Vicente 225, Sala 542L, Gávea, Rio de Janeiro, RJ 22453-900 Brazil; <sup>2</sup>Catholic University/Tecnored, Ltd., R. Gal. Garzon, 22, 308, Rio de Janeiro, RJ 22470010 Brazil

The first part of this work presents the effects of temperature, gas flowrate and external atmosphere over the reduction rates of a carbon composite briquette (CCB), aiming its use as a burden in some of the new alternate ironmaking technologies, such as Tecnored and RHF's. Conversions were obtained determining the metallization degree, being the pre-exponential factor and the apparent activation energy calculated using the Arrhenius equation. It is reported that raises in temperature, decreasing in  $N_2$  flowrate and the use of a  $CO$  atmosphere, increase the reaction rate. Into the second part, a morphological study of the iron metallization process during the reduction of these briquettes is presented. The main objective of this investigation was to assess the morphology of the metallic iron formed into the cross section of the samples, for different temperatures and times of reduction, using Optical and SEM images. It was possible to verify that three types of iron morphology occurred: an external, dense and continuous iron layer, and the presence of iron globules and whiskers at the briquette's core. The measurements of the carbon content on the globules and the external iron layer are also presented.

3:20 PM

**Phase Relations During Sintering of Iron Ore and Fluxing Effect of Minor Components:** *Florian Kongoli*<sup>1</sup>; Ian McBow<sup>1</sup>; Akira Yazawa<sup>2</sup>; <sup>1</sup>FLOGEN Technologies, Inc., Mats. Tech. Dept., 5757 Decelles, Ste. 511, Montreal, Quebec H3S 2C3 Canada; <sup>2</sup>Tohoku University, 16-32, Niizaka, Aoba-ku, Sendai 981-0934 Japan

The production of a homogeneous self-fluxing sinter is an important step in iron making processes. A good sinter should have good permeability and reducibility and has to keep those characteristics for a certain time. An early melt down of the sinter in the blast furnace, where its solid state reduction is essential, would cause many problems such as low permeability and reducibility. Nevertheless, the important factors that influence these characteristics, such as the chemistry of the sinter and the fluxing effect during sintering and sinter reduction conditions, have not yet been clarified. In today's new reality where many new minor components such as  $Al_2O_3$  and  $MgO$  enter to the sinter through raw materials, the quantification of the fluxing effects

during sintering becomes even more important. In this work, the fluxing effect of many sinter major and minor components has been quantified through the characterization of phase relations in the CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at sintering conditions and the quantification of the effect of Al<sub>2</sub>O<sub>3</sub> and MgO by the means of some practical diagrams which can directly help the optimization of the sintering processes.

#### 3:45 PM Break

#### 4:05 PM Invited

**Thermodynamics of Removal of Tramp Elements from Steel Scrap:** *Fumitaka Tsukihashi*<sup>1</sup>; <sup>1</sup>The University of Tokyo, Dept. of Adv. Matls. Sci., Grad. Sch. of Frontier Scis., Tokyo 113-8654 Japan

Increasing amounts of steel scrap are being used as resources for steelmaking. Therefore, there has been a growing interest in the removal of harmful tramp elements such as antimony, zinc, tin, arsenic, bismuth, lead and copper from molten steel. The removal of these elements from molten steel by an oxidative treatment is basically impossible and is feasible by using basic fluxes in a reductive refining process. The problem that should be solved is the removal treatment of tramp elements economically in steelmaking process and production of high quality steel by reducing the effect of contaminated tramp elements with satisfying the environmental issues. In this paper, the available thermodynamic data of the tramp elements in molten steel such as the activities of tramp elements, the partition ratio of them between molten steel and sulfide and calcium based fluxes, and the Gibbs free energy of compounds of tramp elements are summarized. Furthermore, the possibility of the removal of tramp elements from molten steel by using various flux systems is thermodynamically estimated by using these thermodynamic data.

#### 4:35 PM Invited

**Thermodynamics of Mold Powder:** *Hiroyuki Fukuyama*<sup>1</sup>; Kazuhiro Nagata<sup>1</sup>; <sup>1</sup>Tokyo Institute of Technology, Dept. of Chem. & Matls. Sci., 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552 Japan

In continuous casting of steel, mold fluxes play some important roles. In particular, horizontal heat transfer from strand to mold significantly affects surface quality of steel. A crystalline layer in slag films yields larger thermal resistance by scattering infrared radiation from steel and forming air gap at the flux/mold interface. Cuspidine (3CaO·2SiO<sub>2</sub>·CaF<sub>2</sub>) is one of the most important compounds crystallized in slag films during the casting. In order to discuss the crystallization behavior of cuspidine, the present authors have experimentally determined the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> phase diagram around cuspidine. Moreover, the thermodynamic properties of cuspidine are essentially required to discuss the stability field of cuspidine in multi components systems of mold flux. However, no experimental data are currently available on the Gibbs energy of formation of cuspidine. Thus, the present study aims for experimentally determining the Gibbs energy of formation of cuspidine by both electromotive force method and transpiration method.

#### 5:00 PM

**Influence of Reduction-Carburization Conditions on the Rate of Iron Carbide Formation:** *Abdel-Hady El-Geassy*<sup>1</sup>; Mahmoud Ibrahim Nasr<sup>1</sup>; Mohamd Bahgat Sedik<sup>1</sup>; <sup>1</sup>Central Metallurgical Research & Development Institute, Iron-Making Div., PO Box 87-Helwan, Cairo Egypt

High grade iron ore fines rejected from the DRI plants were isothermally reduced in H<sub>2</sub>/CO gas mixtures at 550-850°C. The freshly reduced reaction products were then subsequently carburised in either H<sub>2</sub>/CO or H<sub>2</sub>/CO/S. Thermogravimetric analysis technique was used to follow up both of reduction and carburisation reactions as a function of time. The carburised samples were characterized by X-ray phase identification, Mossbaure and carbon and chemical analyses. The influence of temperature, H<sub>2</sub>:CO ratio in the gas mixtures and carburisation time were intensively investigated and correlated. A conversion extent of iron to Fe<sub>3</sub>C was taken as a measurable index for the efficiency of carburisation reaction under the different experimental conditions. The presence of sulfur greatly stabilize the Fe<sub>3</sub>C formation resulting 96% conversion extent in 40%H<sub>2</sub>/CO mixture at 650°C.

## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Materials Processing Technologies III: Casting and Aluminium Processing

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C5 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Thursday AM  
March 6, 2003

Room: Point Loma  
Location: San Diego Marriott Hotel

*Session Chairs:* W. D. Cho, University of Utah, Dept. of Metallurg. Eng., Salt Lake City, UT 84112 USA; V. M. Kevorkijan, Independent Researching Slovenia

#### 8:30 AM

**Modeling of Melting Behavior of Aluminium Metal in Molten Salt and Metal Bath:** *B. Zhou*<sup>1</sup>; *Y. Yang*<sup>1</sup>; *M. A. Reuter*<sup>1</sup>; <sup>1</sup>Delft University of Technology, Dept. of Appl. Earth Scis., Mijnbouwstraat 120, Delft 2628 RX The Netherlands

During secondary aluminium recovery, complex aluminium scraps are melted and refined often in a rotary melting furnace, and the aluminium metal has to pass through a molten salt layer and melt down in a bottom aluminium bath. An experimental study and industrial observations have indicated that salt shell formation and re-melting on the metal solids in the early stage plays a critical role in the overall melting process of the scrap. In the present paper, mathematical models are developed to simulate the process of salt shell formation and its re-melting, as well as aluminium melting in the molten melt. Influence of the salt layer properties, the residence time of the metal in the salt layer, the particle size and shape, and the temperature of melt were investigated. Reasonable agreement with the measurement data was reached. The developed melting model will be used to construct a population balance model of the scrap melting behaviour for a rotary melting furnace, taking into account the distributed characteristics of the scrap. Finally, an overall process model based on Computational Fluid Dynamics (CFD) for the rotary furnace will be constructed, coupling with the population balance model for the scrap melting.

#### 8:55 AM

**Electrical Noise Analysis of Industrial Aluminium Smelting Cells:** *A. Agnihotri*<sup>1</sup>; <sup>1</sup>Jawaharlal Nehru Aluminium Research Development and Design Centre, Wadi, Nagpur 440023 India

One of the interesting research endeavours in the aluminium reduction industry has been resistance/voltage variation in aluminium reduction pots. Measurement of cell voltage and current simultaneously were conducted in actual plant with high-speed data acquisition system. It was found that the amplitude, frequency, etc. of cell resistance provided valuable information of anode bottom, metal rolling, cell temperature, etc. Special measurements were made in cells at various states of disturbances viz. uneven anode bottom, before anode effect, during anode effect, after anode effect. The resistance/voltage data was analysed at these cell states and electrical noise patterns were studied. The study provided valuable information on cell state by means of data, which is generally averaged out in normal plant operation. Statistical analysis of data obtained provides further scope in evaluating the status of process and detecting operational problems like uneven anode bottom, hydro-dynamic instability, etc. Data analysis deserves more attention as they can be used in predicting the cell stability and operating parameters at very early stage. Details of these are presented in this paper.

#### 9:20 AM

**Theoretical Bases of High-Efficient Purification of Molten Aluminium and Purification Practice:** *Gaosheng Fu*<sup>1</sup>; *Jixing Kang*<sup>1</sup>; *Wenzhe*

Chen<sup>1</sup>; Kuangwu Qian<sup>1</sup>; <sup>1</sup>Fuzhou University, Dept. of Mechl. Eng., Fuzhou 350002 China

In order to obtain aluminum products with higher quality, the harm of metallurgical defects such as inclusions (Al<sub>2</sub>O<sub>3</sub>) and hydrogen must be eliminated or weakened before pouring molten aluminum into mold, because their presence will have direct or indirect influences on strengths, deformation properties and performances of aluminum products. The effective purification treatment of molten aluminum is the key to improving melt cleanness of aluminum. In this paper, based on the analyses of the essences of behavior of inclusions and hydrogen in molten aluminum and their interactive relationship, which are the theoretical bases of high-efficient purification of molten aluminum and are of the utmost importance in determining the technology of purification of molten aluminum, the interactive "parasitic mechanism" between inclusions and hydrogen in molten aluminum is put forward. At the same time, aimed at the currently existing problems in the methods of purification, the principle for purification of molten aluminum, that is, "removing inclusions is the basis for eliminating hydrogen and, therefore, more attention should be firstly paid on removing inclusions" is firstly put forward, thus breaking through the trammel of traditional ideas of purification i.e., more attention is firstly paid on eliminating hydrogen. The principle has been tested and verified in authors' researches and practices. According to this principle above, a new method of purification by filtrating with flux and a corresponding high-efficient flux for removing inclusions have been developed, which has been successfully applied to productions of some high-performance aluminum sheets such as aluminum sheet used for pressure can, etc. It is found that with special flux(CJ-5) for removing inclusions and filtration technology, and proper addition amount and melting temperature, the rate of removing inclusions and the extent of lowering porosity for different grades commercial purity aluminum could amount to about 70-82% and 60-88% respectively, and mechanical properties of this material were improved remarkably, especially the relative increase of elongation(d) was about 70% in comparison to that of no filtration.

9:45 AM

**Original Industrial Application of Two Numerical Models in Concasting Technology:** Frantisek Kavicka<sup>1</sup>; Josef Stetina<sup>1</sup>; <sup>1</sup>Brno University of Technology, Fac. of Mechl. Eng., Technicka 2, Brno 616 69 Czech Republic

Solidification and cooling of a continuously cast slab and simultaneous heating of a crystallizer is a very complicated problem of transient heat and mass transfer. Nowadays, the solving of such a problem is impossible without numerical models of the temperature field not only of the slab itself, while it is being processed through the whole concasting machine (CCM), but of the crystallizer as well. Two original numerical models have been developed and used in the investigation of a continuously cast steel slab. The first (one of two) 3D model of the temperature field of a concasting is capable of simulating the temperature field of a caster. Experimental research and data acquisition have to be conducted simultaneously with the numerical computation-not only to confront it with the actual numerical model, but also to make it more accurate throughout the process. After computation, it is possible to obtain the temperatures at each node of the network, and at each time of the process. The utilization of the numerical model of solidification and cooling of a concasting plays an indispensable role in practice. The potential change of technology-on the basis of computation-is constantly guided by the effort to optimize, i.e. to maximize the quality of the process. The user can therefore choose any appropriate longitudinal or cross-section of a slab and display or print the temperature field in a 3D or 2D graph whenever necessary. The second numerical model of dendritic segregation of elements assesses critical points of slabs from the viewpoint of their increased susceptibility to crack and fissure. In order to apply this model, it is necessary to analyse the heterogeneity of samples of the constituent elements (Mn, Si and others) and impurities (P, S and others) in characteristic places of the solidifying slab. The numerical model, based on measurement results obtained by an electron micro-probe, generates distribution curves showing the dendritic segregation of the analysed element, together with the distribution coefficients of the elements between the liquid and solid states. The combination of both models enables the prediction of cracks and fissures in critical points of the continuously cast carbon-steel slab. Both models had been applied in the industrial investigation of a cast low-carbon-steel slab.

10:10 AM Break

10:30 AM

**Study on the Energy Absorption Property of Foaming Aluminium:** Yihan Liu<sup>1</sup>; Guangchun Yao<sup>1</sup>; Xiaoming Zhang<sup>1</sup>; <sup>1</sup>Northeastern University, Sch. of Matls. & Metall., Shenyang 110004 China

Some different density foaming aluminium samples were prepared in the semi-industrial scale experiment system. Their properties such as energy absorption characteristics, mechanical properties, heat conductivity and acoustical properties were detected. The results showed that the foaming aluminium density from 0.5 to 0.6 g/cm<sup>3</sup> have the better energy absorption, suit to be the ensuring bar of the car, and also suit to be the cushion materials for the engine. The foaming aluminium density from 0.25 to 0.4g/cm<sup>3</sup> have the better acoustical properties and heat conductivity resistance, suit to be the filling material for the door, the ceiling and the partition of the car engine.

10:55 AM

**Study on Formation and Magnetic Susceptibility of Intermetallic Compound Containing Iron, Manganese in the Aluminum Melts:** Guangchun Yao<sup>1</sup>; Linli Wu<sup>1</sup>; Lei Zhang<sup>1</sup>; <sup>1</sup>Northeastern University, The Key Lab. of Electromagnetic Proc. of Matls., Shenyang 110004 China

Iron and silicon impurities would form needle and branch shape intermetallic compounds in the molten aluminum when there was no manganese. It is difficult to separate them from molten aluminum by electromagnetic separation. The Fe-Si-Al and Fe-Al intermetallic compounds were transform into Mn-Fe-Si-Al or Mn-Fe-Al compounds when the manganese was added into the molten aluminum. The metallograph show that the shape of these intermetallic compound particles is lumpish and spherical shape. These impurity particles will suffer less resistance when they were migrated in the molten aluminum and it is benefit to be separated. Some FeSiMnAl<sub>4</sub> and FeMnAl<sub>6</sub> were paramagnetic materials. Their impurity particles could be migrated by the magnetic force and could be separated from the molten aluminum.

11:20 AM

**Study on the Factors Affecting Separation of Iron Impurity from Molten Aluminum by Altering Induced-Magnetic Field:** Guangchun Yao<sup>1</sup>; Lei Zhang<sup>1</sup>; Linli Wu<sup>1</sup>; <sup>1</sup>Northeastern University, The Key Lab. of Electromagnetic Proc. of Matls., Shenyang 110004 China

There are branching and needle-shape intermetallic compounds composed of iron, silicon and aluminum in the molten aluminum. When manganese metal was adding into molten aluminum in a suitable proportion, the shape of the intermallic compound particles may become lumpish and spherical. Depend on the difference of these impurity particles and molten aluminum in electric and magnetic properties, these impurity intermetallic compound particles can be separated by altering magnetic field. In this experiment the altering magnetic field was formed by a "C" type loop which AC (500Hz) current went through. The inner vacuum of the separator made of fireclay refractory materials was 25×15×130mm<sup>3</sup> with a lateral baffle inside. The separator was put into the interspace of the "C" type loop. The experiments of separating iron-rich impurity particles were conducted in different separate time, magnetic intensity and adding manganese respectively. It was found that the longer the separating time was the larger transfe rred amount of impurities would be within three minutes, the transferred amount of impurities increased with the magnetic field intensity strengthened, the separating impurities effect from molten aluminum was increased obviously by adding manganese metal.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Experimental Techniques

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

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Thursday AM  
March 6, 2003

Room: Solana  
Location: San Diego Marriott Hotel

*Session Chairs:* Roberto Parra, Universidad de Concepción, Dept. of Metallurg. Eng., Concepción Chile; Takeshi Azakami, Saitama Institute of Technology, Mechl. Eng., Saitama Japan

8:30 AM

**Recent Progress in Thermal Diffusivity Measurement of Molten Oxides by the Laser Flash Method:** *Hiromichi Ohta*<sup>1</sup>; *Shibata Hiroyuki*<sup>2</sup>; *Yoshio Waseda*<sup>2</sup>; <sup>1</sup>Ibaraki University, Dept. of Matls. Sci., Hitachi 316-8511 Japan; <sup>2</sup>Tohoku University, Inst. of Multidisciplinary Rsrch. for Adv. Matls. (IMRAM), Sendai 980-8577 Japan

Precise thermal properties of molten materials are essentially required for analyzing the process control in metal production. These properties are also important as a clue to consider the dynamic structure of liquid materials. However, it is difficult to obtain the precise thermal diffusivity values of molten materials at high temperature because of the effect of bubble formation and the severe separation of radiative and conductive heat components. We have developed many types of laser flash technique to measure thermal diffusivity of molten oxide such as three layered cell system composed of metal plate/liquid phase/metal crucible, two layered cell system of liquid phase/metal crucible and differential data analysis to estimate the sample thickness as well as radiative heat flow. The main purpose of this paper is to present a novel experimental technique recently developed for measuring thermal diffusivity of molten oxides at high temperatures. In this new technique, the sample is melted in a metal crucible and heated to the desired temperature. A single laser pulse is flashed on the bottom of the crucible and infrared ray irradiated from the same bottom surface is measured for obtaining the temperature decay from which thermal diffusivity of the liquid sample can be estimated. The validity of this new laser flash technique has been confirmed by obtaining the thermal diffusivity values of silicate melts in the temperature range between 773 and 1673 K.

8:55 AM

**Two Methods for the Continuous Measurement of Slag Viscosity from the Glassy to the Liquid States:** *Yutaka Shiraishi*<sup>1</sup>; *Yutaka Sakurai*<sup>1</sup>; <sup>1</sup>AGNE Gijyutsu Center, Ltd., Minami-Aoyama 5-1-25, Kitamura Bldg., Minato-ku, Tokyo 107-0062 Japan

Two methods were developed to measure the viscosity of slag from the glassy to the liquid states in an ascending temperature process. The first method, referred to as the sp method, employs rotating parallel plates within which is placed a solid cylindrical sample in line with a sphere. The viscosity of the glass sample is first determined from the rate of penetration of the sphere into the sample. After the sphere is fully immersed within the sample, the viscosity is determined from the creep rate of the sample between the parallel plates. In the liquid state, the viscosity is determined from the torque generated by the rotation of the plates. The second method, referred as the tp method, uses a tube which is pushed into a sample held in a rotating crucible. In this case, the viscosity is determined from the rate of penetration of the tube into the glass sample and from the torque exerted on the tube by the rotation of the liquid sample. Both methods were tested using standard glasses, including boron trioxide and NBS standard glass #711. The main difference between these two methods is in sample preparation. Comparative measurements between the sp and the tp methods were performed using a sodium boro-di-silicate glass containing 5%mol of alumina. The results showed good agreement in the mid-range of glassy viscosities, 105 to 107 Pa.s. In the liquid state, there were no significant differences between the two methods. A discussion is presented about the observed discrepancies in the results.

9:20 AM

**Advanced Image Analysis of Molten Slag for Process Control:** *Subagyo*<sup>1</sup>; *G. A. Brooks*<sup>1</sup>; <sup>1</sup>McMaster University, Matls. Sci. & Eng., 1280 Main St. W., Hamilton, Ontario L8S 4L7 Canada

The condition of slag in a metallurgical reactor is vital to ensuring control of the process. A new technique based on multivariate image analysis (MIA) of digital images processing has been developed to provide an online measurement of important slag characteristics, such as the presence of exposed metal, the presence of solid phases, and temperature. This paper shall describe the technique and provide some results from plant trials.

9:45 AM

**Impurity Removal from Carbon Saturated Liquid Iron Using Lead Solvent:** *Katsunori Yamaguchi*<sup>1</sup>; *Yoichi Takeda*<sup>1</sup>; <sup>1</sup>Iwate University, Fac. of Eng., Ueda 4-3-5, Morioka, Iwate 020-8551 Japan

A new technique for the removal of tramp-elements from steel scrap has been required from the viewpoint of saving energy and protection of environment. In order to obtain fundamental information on the removal of copper, tin and zinc from molten iron, the extraction method by using of phase separation in the liquid Fe-C-Pb system was investigated at 1453K. A mixture of iron, lead and carbon melted in a carbon crucible separates into two phases of lead and iron containing carbon. The compositions on the miscibility gap in the Fe-C-Pb system are 95.4%Fe-4.5%C-0.1%Pb and 99.9%Pb-0.1%Fe. The

distribution ratios of copper, tin and zinc between the lead and the iron phases,  $LX=[\text{mass}\%X]_{\text{Pb}}/([\text{mass}\%X]_{\text{Fe}})$ , are 2.2, 2.1 and 1.4, respectively. Seventy percent of copper and tin from iron scrap can be eliminated with comparable lead addition.

10:10 AM Break

10:30 AM

**The Criteria of Hydrogen and Oxygen Potentials in Copper Melt for Making a Sound Casting of Bar and Rod—The Guide of the Effective Use of an Electrochemical Gas Monitoring System:** *Norihiko Fukatsu*<sup>1</sup>; *Noriaki Kurita*<sup>1</sup>; *Daisuke Yamamoto*<sup>2</sup>; <sup>1</sup>Nagoya Institute of Technology, Dept. Matls. Sci. & Eng., Gokiso-cho, Showa-ku, Nagoya 466-8555 Japan; <sup>2</sup>Mizuno Corporation, Miyahara-cho, Omiya 330-0038 Japan

The in-line monitoring of the hydrogen and oxygen potentials in molten copper has been realized by using the electrochemical sensors based on the proton and the oxide ion conducting solid electrolyte. In order to use this sensing system effectively, the criteria of the potentials for making sound casting must be known. In the present work, the copper melt equilibrated with a given hydrogen and oxygen potentials was quenched in the crucible. The relations between the holding potentials and the gas porosity in the solidified sample were investigated by measuring the density of the sample and microscopic observations. The criteria thus determined were examined with reference to the measured potentials in the practical casting machine. In tough-pitch copper casting, the problem due to gas porosity was found to be serious when the hydrogen potential increased. In the oxygen-free copper casting, the evolution of hydrogen was found not to be avoided. The gas porosity in the casting, however, was found to be eliminated when the oxygen potential was kept at a low value.

10:55 AM

**Viscosities of FeO-MgO-SiO<sub>2</sub> and FeO-MgO-CaO-SiO<sub>2</sub> Slags:** *Xi Dai*<sup>1</sup>; *Xueping Gan*<sup>1</sup>; *Chuanfu Zhang*<sup>1</sup>; <sup>1</sup>Central South University, Sch. of Metallurg. Sci. & Eng., Changsha, Hunan 410083 China

In the present work, the viscosities of molten FeO-MgO-SiO<sub>2</sub> and FeO-MgO-CaO-SiO<sub>2</sub> semi-synthetic slags at nickel flash smelting conditions were measured in the temperature range from 1523 to 1723 K using a rotational viscometer. The Fe/SiO<sub>2</sub> ratio was maintained constant at 1.2 and the calcium and the magnesium oxide contents were varied in the range from 2 to 8 wt-% and 9 to 12 wt-%, respectively. The viscosity values are presented as a function of temperature and composition.

11:20 AM

**Measurement of the Oxygen Potential of Non-Ferrous Slags with an Ex-Situ Electrochemical Device:** *Nele Moelans*<sup>1</sup>; *Bert Coletti*<sup>1</sup>; *Bart Blanpain*<sup>1</sup>; *Patrick Wollants*<sup>1</sup>; *Jaak Plessers*<sup>2</sup>; *Marc Straetemans*<sup>2</sup>; <sup>1</sup>Katholieke Universiteit Leuven, Dept. of Metall. & Matls. Eng., Kasteelpark Arenberg 44, Leuven B-3001 Belgium; <sup>2</sup>Heraeus Electro-Nite Int. N.V., Centrum Zuid 1105, Houthalen B-3530 Belgium

A measurement method using an ex-situ electrochemical measurement device was developed to determine the oxygen potential of non-ferrous metallurgical slags. The electrochemical cell consists of the molten slag sample, an inert Ir electrode, a stabilized ZrO<sub>2</sub> solid electrolyte, and a Ni/NiO reference electrode. Different slags obtained from non-ferrous pyrometallurgical processes were analysed at 1100 and 1200°C and  $p(\text{O}_2)$  values between  $2 \cdot 10^{-3}$  and  $1 \cdot 10^{-12}$  were obtained. The measurement values were evaluated with thermodynamic calculations and using processing considerations. It was found that the reproducibility and stability of the measurement was significantly improved with the addition of carbon to the slag, especially for slags with a low oxygen potential.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Copper IV

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2C3 Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Thursday AM                      Room: Santa Rosa  
March 6, 2003                      Location: San Diego Marriott Hotel

*Session Chairs:* Susumu Okabe, Mitsubishi Materials Corporation, Tokyo 100-8117 Japan; Florian Kongoli, FLOGEN Technologies Inc., Matls. Tech. Dept, Montreal, Quebec H3S 2C3 Canada

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### 8:30 AM

**Application of Porous Plug System in Anode Furnace, Onsan Smelter:** *Sang-Su Lee*<sup>1</sup>; Baek-Sang Kim<sup>1</sup>; Sei-Phim Choi<sup>1</sup>; <sup>1</sup>LG-Nikko Copper, Inc., Daejung-Ri 70, Ulju-Gun, Onsan-Eup, Ulsan City 689-892 Korea

This paper shows the application of porous plug system in the Mitsubishi continuous copper smelting and converting process. This system has already adopted and utilized in the steel industry to enhance productivity. Recently, some copper smelter has adopted this system but the result has not been satisfactory. Porous plug system was installed at the Anode furnace in December 2001 to reduce oxidation time and decrease the oil consumption. Some good effect is that nitrogen stirring the melt through porous plugs, improved the heat transfer of the melt. As the result of enhancing heat transfer, oil consumption and inside build-up was actually decreased. But the oxidation time has not sufficiently been reduced until now. In the future, further research and local test is needed for productivity increase and cost saving.

### 8:55 AM

**Behavior of Silver in the Electric Furnace for Copper Dross Treatment:** *Takao Yasugi*<sup>1</sup>; <sup>1</sup>Toho Zinc Company, Ltd., Production Dept., 5562-1 Higashino-cho, Toyota-gun, Hiroshima-Pref. 725-0222 Japan

The majority of copper in the raw material migrates to the decopperized dross formed when crude lead produced from the blast furnace is treated by the decopperizing process. Decopperized dross is treated in the electric furnace, producing crude lead, matte, and speiss. Decopperized dross contains large amounts of silver. Therefore, it is important to improve the rate of silver migration to crude lead. For this reason, we examined the behavior of silver between the crude lead, speiss, and matte phases. At the same time, we conducted several tests to improve the percentage of silver migrating to crude lead.

### 9:20 AM Invited

**A Process Designed for the Ancient Copper Smelting Slags:** *Bora Derin*<sup>1</sup>; *Onuralp Yücel*<sup>1</sup>; Ercan Acma<sup>1</sup>; Okan Addemir<sup>1</sup>; <sup>1</sup>Istanbul Technical University, Metallurg. & Matls. Dept., Fac. of Cheml. & Metallurgl. Eng., Maslak, Istanbul 80626 Turkey

This work carried out on the ancient copper smelting slags located in Küre-Turkey for recovery of valuable metals. In this process, copper and cobalt were recovered as metallic and their components, where as iron was recovered as magnetic oxide or pigment from the slag. The process stages were involved carbothermal reduction in DC-Arc Furnace, leaching, chemical precipitation, selective roasting and product preparation. In this paper, the process stages were described as theoretically and experimentally where as slag and products were characterized in detail.

### 9:45 AM

**Present and Future of Caletones Smelter:** *Patricio Burchard Chacana*<sup>1</sup>; *Gerardo Hernán Achurra*<sup>1</sup>; Julio Gatica Buchi<sup>1</sup>; Fernando Andres Condore<sup>1</sup>; <sup>1</sup>CODELCO, El Teniente, Caletones Smelter, Millan 1020, Rancagua, O'Higgins VI 000 Chile

During the last years, Caletones Smelter like others world copper smelter, has evolved from conventional, inefficient, pollutant and expensive technologies, to modern, environmentally friendly and efficient ones. For it and besides for improving its competitive position, in the last period this Smelter shut down their reverberatory furnace, started up two big acid plants and has developed some pyrometallurgical technologies. The main facilities of Caletones Smelting and Converting Process, in the present and future, are the Teniente Converters, reactors with a high operational availability that have reached concentrate top process capacities near to 2,400 T/D. These reactors operate in most of the Chilean smelters as well as in other world smelters: Zambia, Peru and Mexico. Since 2000, the Caletones Smelting and Converting Process, has been performed in two Teniente Converters, four Slag Cleaning Furnaces and four Pierce-Smith Converters. These facilities, together with the operation of two Fluidized Bed Dryers and two Oxygen Plants have allowed to reach concentrate melting capacities and copper productions of 1,250 KDT/year and 380 KFT/year, respectively. Associated to El Teniente Division Expansion Plan, in a first stage, Caletones Smelter will increase its capacity to 1,440 KT/year the 2004. In the long term, Caletones has different options, from 1,600 to 2,000 KT/year, producing anodes, white metal or a mixture of them. This options are connected with CODELCO's Smelters & Refineries Strategic Plan, including Mejillones Project. The main challenges of Caletones Smelter are associated to develop and consolidate Continuous and Environmental Friendly Processes, automation and control of different processes and improve its leadership between World Copper Smelters.

### 10:10 AM Break

### 10:25 AM Invited

**Thermodynamic Fundamentals of Calcium Ferrite Slag and their Application to Mitsubishi Continuous Copper Converter:** *Fumito Tanaka*<sup>1</sup>; Osamu Iida<sup>2</sup>; Yoichi Takeda<sup>3</sup>; <sup>1</sup>Mitsubishi Materials Corporation, Central Rsrch. Inst., 1-297 Kitabukuro-cho, Saitama 330-8508 Japan; <sup>2</sup>Mitsubishi Materials Corporation Metals Company, Process & Tech. Dept., 1-5-1 Ohtemachi, Chiyoda-ku, Tokyo 100-8117 Japan; <sup>3</sup>Iwate University, Dept. of Matls. Sci. & Tech., 4-3-5 Ueda, Morioka, Iwate 020-8551 Japan

The Mitsubishi process is the sole pyrometallurgical process for continuous production of blister copper from copper concentrates and has been successfully operated around the world. The development of calcium ferrite slag (CaO-FeOx-Cu<sub>2</sub>O), so called "C-slag", has enabled continuous converting from matte to blister copper in commercial scale operation. Commercial interests in the slag led to many papers over CaO-FeOx slag. However, Cu<sub>2</sub>O-bearing slag has not been studied well due to experimental difficulties. The authors have quantified thermodynamic properties of CaO-FeOx-Cu<sub>2</sub>O system. The results have been utilized to analyze various issues related to the converting furnace, such as magnetite precipitation from slag or from blister copper, and to develop better control criteria for the continuous converting operation.

### 10:50 AM

**Process Development, Optimization and Automation through Appropriate Thermophysicochemical Modeling and Simulation Software:** *F. Kongoli*<sup>1</sup>; I. McBow<sup>1</sup>; S. Llubani<sup>1</sup>; <sup>1</sup>FLOGEN Technologies, Inc., 5757 Decelles Ave., Ste. 511, Montreal, Quebec H3S 2C3 Canada

Nonferrous and ferrous smelting industries have recently faced the unavoidable necessity of changing and/or improving the smelting technologies as a result of the use of new raw materials which are becoming available from different geographical areas. These new feed materials usually contain different ore composition and higher level of minor components, which adversely affect the smelting process. Due to the problems encountered in several processes as a result of this feed diversification some work has been undertaken in order to make uniform the feed and avoid later surprises in the smelting process. However this has proven to be very difficult and sometimes almost impossible. In this work a more viable approach is undertaken to deal with this problem. It consists of controlling not the cause of the problem i.e. the feed composition but instead the results of this feed change, i.e. the end-point of smelting technologies. It is shown that this approach, when carried out through appropriate thermophysicochemical modeling and simulation software is not only easier and less costly but it also helps the automation of the smelting process. Several examples are given and future work is underlined.

### 11:15 AM

**Control of Magnetite Behavior in the Mitsubishi Process at Naoshima:** *Nozomu Hasegawa*<sup>1</sup>; Hideya Sato<sup>1</sup>; <sup>1</sup>Mitsubishi Materials Company, Ltd., Naoshima Smelter & Refinery, 4049-1 Naoshima-cho, Kagawa-Gun, Kagawa 761-3110 Japan

The phase diagrams and microstructures of slags in the Mitsubishi Continuous Copper Smelting and Converting Process were studied for the prevention of magnetite troubles such as accretion build-up on furnace hearths and launders, melt outlet blockages, slag viscosity increases and so on. According to the result of those studies, the silica and lime content in the silicate slag at the smelting furnace and the lime content in the calcium-ferrite slag at the converting furnace were changed, and then the slag loss of copper in the discard slag has been stabilized lower than before and the cleaning- frequency of melt outlets and launders has been significantly reduced. However, those procedures may decrease the desirable amount of accretion-coating inside the furnaces and thereby reduce the furnace campaign lives. Therefore, an estimating method of those accretion amounts was developed, and slag compositions and temperatures have been controlled within the appropriate ranges to prolong furnace lives and also prevent magnetite troubles.

#### 11:40 AM

**The Behavior of Impurities at Kosaka Smelter:** *Satoshi Nakagawara*<sup>1</sup>; Kenji Watanabe<sup>2</sup>; <sup>1</sup>Kosaka Smelting & Refining Company, Ltd., Production Mgmt. Sec., 60-1 Otarube, Kosaka, Kazuno, Akita 017-0202 Japan; <sup>2</sup>Kosaka Smelting & Refining Company, Ltd., Techn. Dept., Kosaka, Kazuno, Akita 017-0202 Japan

Kosaka Smelter has been changed to a custom smelter and devoting to treat the complex sulfide copper concentrates in the world. Since the mid-80s, a progressive diversification of the smelter input has taken place, impure and complex sulfide concentrate being introduced in increasing proportions compared with the period of the "Black Ore" treatment. And recently, Kosaka is trying to add value to its copper smelting by recovering valuable metals from non-concentrate materials (e.g., recycled materials and the residue generated in the zinc smelter), and by increasing the volume of recovery. In this process, precious metals are mostly recovered and unnecessary impurities are efficiently removed. Thus, it can be said that recent operation of Kosaka Smelter depends on the treatment of impurities. This is a report on the behavior of impurities at Kosaka Smelter which performs outstanding smelting operation.

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## Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Iron and Steel Making Fundamentals III and Applications

*Sponsored by:* Extraction & Processing Division, EPD-Process Fundamentals Committee, EPD-Pyrometallurgy Committee, EPD-Aqueous Processing Committee, EPD-Copper, Nickel, Cobalt Committee, EPD-Lead and Zinc Committee, Jt. MPMD/EPD-Process Modeling Analysis & Control Committee; See Plenary Session for Co-Sponsors

*Program Organizers:* Hong Yong Sohn, University of Utah, Department of Metallurgical Engineering, Salt Lake City, UT 84112-0114 USA; Kimio Itagaki, Tohoku University, Institute for Advanced Materials, Sendai 980-8577 Japan; Florian Kongoli, FLOGEN Technologies, Inc., Materials Technology Department, Montreal, Quebec H3S 2CS Canada; Chikabumi Yamauchi, Nagoya University, Department of Materials Science & Engineering, Nagoya 464 8603 Japan

Thursday AM                      Room: Leucadia  
March 6, 2003                      Location: San Diego Marriott Hotel

*Session Chairs:* H. G. Kim, POSCO Research Institute Korea; Varadarajan Seshadri, Universidade Federal de Minas Gerais, Dept. of Metallurg. Eng. & Matls., Belo Horizonte Brazil

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#### 8:30 AM Invited

**Operational Improvements for RH-KTB Degasser of Companhia Siderurgica De Tubarao (CST) Steel Plant Through a Physical Modeling Study:** *Varadarajan Seshadri*<sup>1</sup>; Itavahn Alves da Silva<sup>2</sup>; Carlos Antonio da Silva<sup>2</sup>; Roberto Parreiras Tavares<sup>1</sup>; Ernane Márcio de Castro Martins<sup>3</sup>; Fernando Demuner da Silva<sup>1</sup>; Geraldo Alves Vargas Filho<sup>4</sup>; Paulo Sérgio Bringhamti Lascosqui<sup>4</sup>; <sup>1</sup>Universidade Federal de Minas Gerais, Dept. of Metallurg. Eng. & Matls., Belo Horizonte Brazil; <sup>2</sup>Universidade Federal de Ouro Preto, Dept. of Metallurg. & Matls. Eng., Ouro Preto Brazil; <sup>3</sup>Universidade Federal de Ouro Preto, REDEMAT, Ouro Preto Brazil; <sup>4</sup>Companhia Siderurgica de Tubarão, Vitoria Brazil

Improvements in the efficiency of the metallurgical performance of refining reactors in the metallurgical industry can be achieved through physical modeling of the unit and experimentation in the laboratory scale. In the Rh process, macroscopic parameters such as circulation time and mass transfer coefficient for the degassing step are important parameters which decide improved operational practice. In this study the effect of some operational parameters, such as diameter of snorkels, gas injection flow rate through bottom of the ladle, gas flow rate through nozzles on the circulation rate and decarburization of steel are investigated using a physical model. The object of the investigation was to improve the performance characteristics of the RH-KTB degasser of Companhia Siderurgica de Tubarão (CST) steel plant.

#### 9:00 AM

**Optimization of the Injection Refining-Up Temperature Process (IR-UT) of the Companhia Siderurgica de Tubarao Steel Plant (CST) Using Physical Modeling:** *Carlos Antonio da Silva*<sup>1</sup>; Itavahn Alves da Silva<sup>1</sup>; Varadarajan Seshadri<sup>2</sup>; Cristiano Magson de Oliveira Genelhu Silva<sup>3</sup>; Marcos de Paula Alves<sup>1</sup>; Carlos Alberto Perim<sup>4</sup>; <sup>1</sup>Universidade Federal de Ouro Preto, Dept. of Metallurg. & Matls. Eng., Ouro Preto Brazil; <sup>2</sup>Universidade Federal de Minas Gerais, Dept. of Metallurg. Eng. & Matls., Belo Horizonte Brazil; <sup>3</sup>Universidade Federal de Ouro Preto, REDEMAT, Ouro Preto Brazil; <sup>4</sup>Companhia Siderurgica de Tubarão (CST), Vitoria Brazil

Steel refining reactors based on chemical heating are being used as an alternative to ladle furnaces. They show a high degree of flexibility in respect of heating rate in addition to the ease in carrying out refining reactions such as desulphurization, inclusion removal, alloying etc. IR-UT and CAS-OB are examples of such reactors. Their performance is dependent upon geometrical characteristics as well as operational conditions which determine the flow field inside the vessel. A physical model of the IR-UT process of the Companhia Siderurgica de Tubarão steel plant situated in Vitoria, Brazil was developed to assess the features of the flow field and its influence on the metallurgical behavior. Results of the physical model were used to optimize the process parameters.

#### 9:25 AM

**Effect of TiC Addition on Corrosion Resistance of MgO-C Based Refractories to Smelting Reduction Slag:** *Qingcai Liu*<sup>1</sup>; Jing Lin<sup>1</sup>; Dengfu Chen<sup>1</sup>; Joseph W. Newkirk<sup>2</sup>; <sup>1</sup>Chongqing University, 174 Shapinba St., Chongqing 400044 China; <sup>2</sup>University of Missouri-Rolla, 1870 Miner Cir., Rolla, MO 65409 USA

The interaction between MgO-C-TiC refractories and slag of smelting reduction with and without iron bath was studied by rotary immersion and stationary immersion test. The effects of the TiC addition to the corrosion behavior of the MgO-C based refractories were investigated in detail. The present work highlights significant improvements in the corrosion resistance of the refractories to slag from addition TiC in the MgO-C based refractories. Petrographic and SEM analysis of the refractories after the slag test show that TiC increases the viscosity of both the glassy phase of the refractory and the slag film. This effect retards the slag penetration into refractory and the interaction between the slag film and the deterioration layer of refractory.

#### 9:50 AM

**Assessment of the Performance of the Tundish of a Six Strand Continuous Casting Unit of Companhia Siderurgica de Belgo Mineira(CSBM) Using Physical Modeling:** *Mônica Suede Santos Silva*<sup>1</sup>; Elvis Gonçalves da Mota<sup>2</sup>; Edilson Caniçali Fracalossi<sup>2</sup>; Carlos Antônio da Silva<sup>2</sup>; Itavahn Alves da Silva<sup>2</sup>; Joaquim Gonçalves da Costa Neto<sup>3</sup>; Varadarajan Seshadri<sup>4</sup>; <sup>1</sup>Universidade Federal de Ouro Preto, REDEMAT, Ouro Preto Brazil; <sup>2</sup>Universidade Federal de Ouro Preto, Dept. of Metallurg. & Matls. Eng., Ouro Preto Brazil; <sup>3</sup>Companhia Siderurgica de Belgo Mineira, João Monevalde Brazil; <sup>4</sup>Universidade Federal de Minas Gerais, Dept. of Metallurg. Eng. & Matls., Belo Horizonte Brazil

This work describes characterization of the performance of the tundish of a six strand continuous casting unit of the Companhia siderurgica Belgo Mineira, João Monlevade, Brazil using physical modeling. Permanent and transient conditions, due to ladle metal composition changes are considered. Pulse and step tracer addition techniques are employed to assess the control variables. For transient conditions the degree of inter-mixing and the minimum residence time are determined with a view to optimizing the process especially during the grade changes of steel.

#### 10:15 AM Break

#### 10:25 AM

**Interfacial Area in Pyrometallurgical Reactor Design:** *Geoffrey Alan Brooks*<sup>1</sup>; Subagyo<sup>1</sup>; <sup>1</sup>McMaster University, Dept. of Matls. Sci. &

Eng., 1280 Main St. W., Hamilton, Ontario L8S4L7 Canada

Increasing interfacial area through gas injection is one of the main methods for accelerating reaction between slag, metals and gases in modern metallurgical reactors. This paper will examine the limitations of top lance and bottom tuyere blowing in terms of interfacial area generation and examine alternative reactor designs that may overcome these limitations. The effect of the quantity and size of droplets generated through gas injection on overall reactor design performance, especially relating to settling rates, will be examined in this paper.

**10:50 AM**

**Software for Selection and Analysis of Mould Fluxes for Continuous Casting of Slabs:** *Fabricio Batista Vieira*<sup>1</sup>; Varadarajan Seshadri<sup>2</sup>; Roberto Parreiras Tavares<sup>2</sup>; <sup>1</sup>Vallourec & Mannesmann Tubes, Belo Horizonte, MG 30640-010 Brazil; <sup>2</sup>Federal University of Minas Gerais, Metallurg. & Matls. Eng. Dept., Belo Horizonte, MG Brazil

Mould fluxes are synthetic slags normally used in continuous casting of steels, particularly in slab casting. They should satisfy several requirements, which include: - reducing the friction between the strand and the mould walls; - controlling the heat transfer between the solidified shell and the mould. The performance of mould fluxes in satisfying the requirements above can have a significant effect on the efficiency of the continuous casting process and on the surface quality of the products. This performance is affected by various parameters including the characteristics of the mould fluxes, the quality of the steel being cast and the operational conditions of the caster. The extremely complex relationships involving the parameters mentioned above make it very difficult to have simple criteria for selecting mould fluxes for casting a certain grade of steel in a continuous casting machine. These difficulties led steelmakers and mould flux suppliers to select mould fluxes based mainly on plant trials. In the present work, a software to help in the analysis and development of mould fluxes for continuous casting was developed. This software includes several models for prediction of mould flux viscosity and consumption. A mathematical model was also used to predict the heat flux through the mould flux. The proposed methodology was applied to continuous casting of crack sensitive steels. Some of the results given by this software are presented, discussed and compared to plant data.

**11:15 AM Invited**

**Modeling of EAF Slag Chemistry for Optimal Slag Foaming and Refractory Service Life:** *James P. Bennett*<sup>1</sup>; Kyei-Sing Kwong<sup>1</sup>; <sup>1</sup>USDOE, Albany Rsrch. Ctr., 1450 Queen Ave. SW, Albany, OR 97321 USA

EAF slag chemistry and its control have been recognized as important in producing quality steel at a low price for a number of decades. EAF steel producers make lime and dolomite additions to furnaces, controlling the C/S ratios and sulfur pickup from the steel. Existing phase diagram data at 1600°C for CaO, MgO, FeO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> was used to write a computer model optimizing slag chemistry for slag foaming and reduced refractory wear. The model, its development, and its use in an industrial steelmaking environment will be discussed along with how the model can improve energy efficiency. The importance of EAF mass balance to account for critical materials like Si in scrap and refractory wear using the model will also be emphasized.

## ADDENDUM

Page 7: Session

**Yazawa International Symposium on Metallurgical and Materials Processing: Principles and Technologies: Advances in Non-Ferrous Production Technologies and Industrial Practice: Nickel**

Monday PM            Room: Santa Rosa  
March 3, 2003        Location: San Diego Marriott Hotel

**2:30 PM:** Paper will be presented at 2:55 PM at the same session

**2:55 PM:** Paper will be presented at 4:20 PM at the same session

**4:20 PM:** Paper is replaced with the following one and will be presented at 2:30 PM at the same session:

**Technology Development and Metallurgical Improvements of an Inco Flash Furnace Process Treating Copper-Nickel Concentrates:**  
W.G. Bacon<sup>1</sup>, M.O. Fezzani<sup>1</sup>, Randy E. Lawson<sup>2</sup>, W.P. Lee<sup>1</sup> :<sup>1</sup>Inco Technical Services Limited 2060 Flavelle Boulevard Mississauga, Ontario, Canada L5K 1Z9; <sup>2</sup>Ontario Division Copper Cliff Smelter Complex, Copper Cliff, Ontario, Canada, P0M 1N0

Desirable features of the Inco flash furnace (FF), through the decades, made it the technology of choice to treat a combined Cu-Ni (bulk) concentrate as part of Inco's SO<sub>2</sub> Abatement Program (SOAP project) completed in 1993 resulting in two new larger Inco FF's. The flowsheet developed for the smelting of bulk concentrates necessitated some important process changes to the original copper smelting furnace, mainly brought about by downstream process constraints. Today in the Sudbury smelter, the process flowsheet employing the Inco bulk flash furnace features:

- Additional fuel requirements owing to the non-autogenous furnace matte grade.
- All furnace gases fixed with no fixation of converter offgases.

As part of the continuous process improvement objectives carried out by Inco's corporate technical center (ITSL) and in anticipation of further reductions in SO<sub>2</sub> emissions, ITSL has been developing alternative operating schemes for the Inco flash smelting process. The evolution of these alternatives was brought about through a combination of applied bench scale research, miniplant and commercial scale testing. An example of such a project is given here as a case study, which indicates how the usually conflicting goals of reducing SO<sub>2</sub> emissions while simultaneously improving process economics may be achieved.