

Rare Metal Technology

2014

Editors

Neale R. Neelameggham

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Rare Metal Technology

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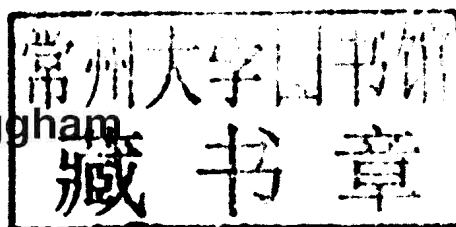
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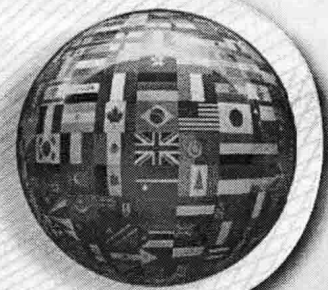
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PREFACE

Rare Metal Technology 2014 is the proceedings of the symposium on Rare Metal Extraction & Processing, which was initiated by the Hydrometallurgy and Electrometallurgy Committee of the Extraction & Processing Division (EPD) of TMS (The Minerals, Metals & Materials Society). The Pyrometallurgy Committee of EPD is a co-sponsor of this symposium. The following international metallurgical societies are also co-sponsors of this symposium: Associação Brasileira de Metalurgia, Materiais e Mineração – ABM, Chinese Society for Metals, The Metallurgy and Materials Society of CIM, and The Institute of Materials, Minerals and Mining. The symposium has been organized to encompass the extraction of rare metals as well as rare extraction processing techniques used in metal production.

The intent of the symposium was to avoid conflicts with major international symposiums during 2013–2014 such as the International Hydrometallurgy Conference and International Precious Metals Conference, while covering the extraction of rare metals, that is, less common metals or minor metals, not covered by other TMS symposia. The elements considered included antimony, bismuth, barium, beryllium, boron, calcium, chromium, gallium, germanium, hafnium, indium, manganese, molybdenum, platinum group metals, rare earth metals, rhenium, scandium, selenium, sodium, strontium, tantalum, tellurium, tungsten, etc. These are rare metals of low-tonnage sales compared to high-tonnage metals such as iron, copper, nickel, lead, tin, and zinc; or light metals such as aluminum, magnesium, or titanium and electronic metalloid silicon. Rare processing includes bio-metallurgy, hydrometallurgy, and electrometallurgy, as well as extraction of values from EAF dusts and less-common waste streams not discussed in recycling symposiums. Rare high-temperature processes represented in this volume include microwave heating, solar–thermal reaction synthesis, and cold crucible synthesis of the rare metals and the design of extraction equipment used in these processes as well as laboratory and pilot plant studies.

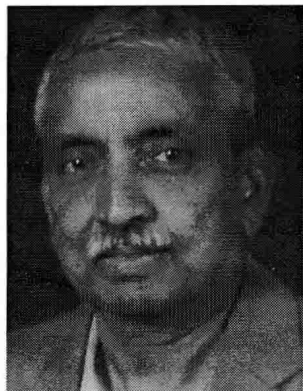
The present proceedings cover about 20 rare metal elements and 15 rare earth elements. Uses of orange juice waste and shellfish waste in extractive metallurgy benefit the rare processing title. Recovery of rare elements includes recoveries of indium from LCD monitors and other recycling of rare earth elements. The symposium is organized into sessions encompassing:

1. Metalloids and Rare Metal Extraction Process
2. Indium, Moly, and Tungsten Metallurgy
3. Calcium and Rare Earth Metallurgy
4. Titanium, Lithium, Yttrium, and Zirconium
5. Rhenium, Tin, Vanadium, and SX Processing

We appreciate valuable inputs from Tom Battle, Adrian Deneys, Mike Free, V. Ramachandran, and Trudi Dunlap at the initial stages of formulating the symposium and in obtaining co-sponsorship worldwide. We acknowledge the efforts by the organizing and editing team consisting of Neale R. Neelameggham, Shafiq Alam, Harald Oosterhof, Animesh Jha, and Shijie Wang. Our thanks to Trudi Dunlap and Patricia Warren of TMS in assembling the proceedings.

Neale R. Neelameggham

ABOUT THE LEAD EDITOR



Neale R. Neelameggham is “The Guru” at IND LLC, involved in technology marketing and international consulting in the field of light metals and associated chemicals (boron, magnesium, titanium, lithium, and alkali metals), rare earth elements, battery and energy technologies, etc. He has been an advisor in various environmental extractive processes for metal production and energy process firms.

Dr. Neelameggham has more than 38 years of expertise in magnesium production technology from the Great Salt Lake Brine in Utah, involved in process development of its startup company NL Magnesium through the present US Magnesium, LLC, from which he retired. He was involved in most of the process and equipment development of all areas of the plant from the raw material source—the Great Salt Lake Brine, which is concentrated by solar evaporation into a plant feed and further purified—followed by spray drying and preparation of anhydrous magnesium chloride cell feed to electrolytic cells and then into magnesium metal product and chlorine.

In addition, Dr. Neelameggham’s expertise includes an in-depth and detailed knowledge of all competing technologies worldwide of magnesium production, both electrolytic and thermal processes, such as the Pidgeon Process, Murex Process, Zuliani Process, and others, as well as alloy development. This expertise is used in engineering a tailor-made magnesium process to fit any resources and has developed near zero-waste sustainable magnesium production process and equipment. He was a visiting expert at Beihang University of Aeronautics and Astronautics, Beijing, China.

Dr. Neelameggham holds 13 patents and a patent application on boron production and has several technical papers to his credit. As a member of TMS, AIChE, and a former member of American Ceramics Society, he is well versed in energy engineering, bio-fuels, rare-earth minerals and metal processing and related processes. Dr. Neelameggham has served in the Magnesium Committee of the TMS Light Metals Division (LMD) since its inception in 2000, chaired it in 2005, and in 2007 he was made a permanent co-organizer for the Magnesium Technology symposium. He has been a member of the Reactive Metals Committee, Recycling Committee, and Titanium Committee, and has been a Program Committee Representative of LMD. He received the LMD Distinguished Service Award in 2010.

In 2008, LMD and the Extraction & Processing Division (EPD) created the Energy Committee following the CO₂ Reduction Metallurgy Symposium that he initiated. Dr. Neelameggham was the inaugural chair for the Energy Committee and has served as a co-organizer of the Energy Technology symposium since 2008. Dr. Neelameggham holds a doctorate in extractive metallurgy from the University of Utah. He has been selected as the Chair of the Hydrometallurgy and Electrometallurgy Committee of EPD for the 2013-2015 term.

ABOUT THE EDITORS



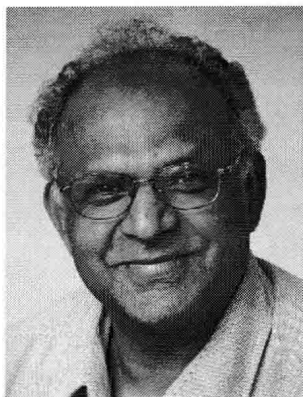
Shafiq Alam is an associate professor at Memorial University of Newfoundland, Canada. In 1998, he received his Ph.D. in Chemical Engineering from Saga University, Japan. From 1999 to 2001, he was appointed as a post-doctoral research fellow at the University of British Columbia and the University of Toronto, Canada.

Dr. Alam has extensive experience in industrial operations, management, engineering, design, consulting, teaching, research, and professional services. Before joining Memorial University in 2006, he worked with many different companies, such as Shell, Process Research ORTECH Inc., in Mississauga, Ontario; Fluor Canada, Ltd., in Vancouver; and the National Institute of Advanced Industrial Science and Technology (AIST) in Japan. Dr. Alam is highly experienced in the area of extractive metallurgy. He is the lead researcher and head of the hydrometallurgy lab at the INCO Innovation Centre (IIC) at Memorial University. He possesses two patents and has more than 80 publications in the area of hydrometallurgy.

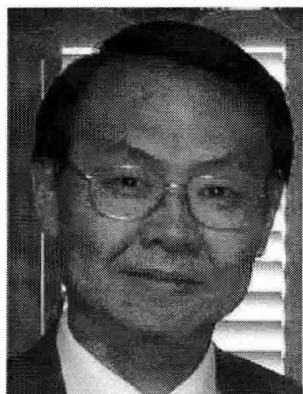
Dr. Alam is a registered professional engineer and has worked on projects with many different mining companies, including Xstrata, Phelps Dodge, INCO, and Barrick Gold Corporation. He is an executive committee member of the Hydrometallurgy Section of the Canadian Institute of Mining, Metallurgy and Petroleum (CIM) and is actively involved with the committee in organizing different international conferences, such as the Conference of Metallurgists (COM) in Canada; Ni-Co Symposium at TMS 2013 in San Antonio, Texas, USA; the Copper 2013 Conference in Chile; and Rare Metal Extraction & Processing Symposium at TMS 2014 in San Diego, California, USA. Currently he is the Vice Chair of the Hydrometallurgy and Electrometallurgy Committee of the Extraction & Processing Division of TMS.



Harald Oosterhof graduated as a chemical engineer from Twente University in The Netherlands in 1994. In the same year, he assumed a position as researcher at TU Delft where he worked in the laboratory for process equipment. His research on anti-solvent crystallization of well-soluble salts was rewarded with two patents and a dozen publications. After receiving his Ph.D. from Delft University in 1999, he assumed the position of project manager at Umicore, a global materials and technology group that is based in Belgium. During his first assignment as Project Leader – Hydrometallurgy, he focused on the refining of cobalt, nickel, and germanium. Since 2011, Dr. Oosterhof has worked as scientist in the Recycling and Extraction Technology group at Umicore's Central R&D department. His main competence areas are special metals hydrometallurgy, recycling and refining of rare earth metals, base metal hydrometallurgy, and recycling of spent rechargeable batteries. In his current job, Dr. Oosterhof is frequently involved in business development of scarce metals recycling and he is heading a team of hydrometallurgical specialists.



Animesh Jha has been serving the University of Leeds since March 1996, where his main research focus is on rare earth minerals and materials and their applications. In this field, his interest is split between chemical processing of rare earth-bearing concentrates and further refining, and rare earth ion-doped optical materials and laser devices. Before joining Leeds, he was lecturer at Brunel University at Uxbridge, UK; a research postdoctoral fellow at the University of Sheffield, UK (from December 1986 to April 1989), and Purdue University, USA (from May 1985 to November 1986). He obtained his Ph.D. from the Imperial College of Science and Technology, University of London, UK in October 1984 in the area of chemical metallurgy. His diploma of Imperial College was in process engineering. He has published more than 250 research articles in peer-review journals and more than 150 articles in conferences, and he has 45 patents as inventor/co-inventor to his credit. He is a fellow of the Institute of Physics since 2010, a member of TMS since 1992, and a member of the Optical Society of America and IEEE since 2000.



Shijie Wang received his B.Sc. in mineral processing from China and his masters and Ph.D. in metallurgical engineering from the University of Nevada at Reno. Dr. Wang has experience working at the Beijing General Research Institute for Non-Ferrous Metals, ASARCO Inc., and Phelps Dodge Corporation. He is currently Principal Advisor at Rio Tinto Kennecott Utah Copper. Dr. Wang has been active in extractive metallurgy and has experience in metallurgical process development and existing operation optimization as well as troubleshooting. His work interests include metal recovery, operational excellence and profitability. Dr. Wang holds three U.S. patents and has published more than 20 journal papers on topics including tellurium and rare earth metals' resourcefulness and recovery. He is a copper, precious metals, and Se/Te refining subject matter expert. Dr. Wang has been a TMS member since 1991.

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Session Chairs

Metalloids and Rare Metal Extraction Process

Shafiq Alam
Katsutoshi Inoue

Indium, Moly, and Tungsten Metallurgy

Shijie Wang
Michael Free

Calcium and Rare Earth Metallurgy

Neale R. Neelameggham
Bing Li

Titanium, Lithium, Yttrium, and Zirconium

M. Ashraf Imam
Di Yuezhong

Rhenium, Tin, Vanadium, and SX Processing

Harald Oosterhof
Brent Hiskey

TABLE OF CONTENTS

Rare Metal Technology 2014

Preface	ix
About the Editors	xi
Session Chairs	xv

Metalloids and Rare Extraction Process

Adsorptive Recovery of Antimony (III, V) Using Metal-loaded Orange Juice Residue	3
<i>K. Inoue, J. Inoue, and S. Alam</i>	
The Synthesis and Stability of Yukonite: Implications in Solid Arsenical Waste Storage	9
<i>M. Bohan, J. Mahoney, and G. Demopoulos</i>	
The Evolving Copper-Tellurium Byproduct System: A Review of Changing Production Techniques & Their Implications	11
<i>M. Bustamante and G. Gaustad</i>	
Conversion of Strontium Sulfate to Strontium Oxalate in Solutions Containing Ammonium Oxalate as a Reactant	17
<i>M. Zoraga, C. Kahruman, and I. Yusufoglu</i>	
Electrodeposition of Zinc from Zinc Oxide Using Urea and Choline Chloride Mixture: Effect of (BMIM)HSO ₄ , Temperature, Voltage on Current Efficiency, Energy Consumption, and Surface Morphology	21
<i>H. Yang and R. Reddy</i>	
Effect of Physical Parameters on the Stirred Separation Process in Rare Earth Extraction System	27
<i>S. Wang, Z. Zhang, T. Zhang, Q. Zhao, Y. Liu, C. Lv, and D. Zhang</i>	
Slurry Electrolysis of As-Rich Antimonite Gold Concentrate Ores	31
<i>C. Wang, Y. Chen, Y. Yang, Y. Zhang, and B. Ma</i>	

Indium, Moly, and Tungsten Metallurgy

Recovery of Rare Metal Indium (In) from Discarded LCD Monitors	39
<i>P. Choubey, M. Jha, D. Gupta, J. Jeong, and J. Lee</i>	
Thermodynamics of Indium Dissolution Behavior in FeO-bearing Metallurgical Slag	43
<i>Y. Han and J. Park</i>	
The Separation of Tungsten and Molybdenum by Ion Exchange Resins	47
<i>G. Huo, C. Peng, and C. Liao</i>	
Removal of Na from the Ammonium Tungstate Solution by NaI+xAlxTi ₂ -x(PO ₄) ₃	53
<i>X. Chen, X. Liu, J. Li, and Z. Zhao</i>	
Removal of Sn from the Tungstate Solution by Nascent Hydrous Ferric Oxide	57
<i>Z. Zhao, X. Chen, X. Liu, and J. Li</i>	
Pressure Water Leaching Molybdenum and Nickel from Mo-Ni Ore of Black Shale without Reagent	61
<i>Z. Deng, C. Wei, C. Li, X. Li, and M. Li</i>	

Calcium and Rare Earth Metallurgy

Calcium Reductants – A Historical Review	67
<i>N. Neelameggham, R. Brown, and B. Davis</i>	
Research on the Electrochemical Behavior of CaO in CaCl ₂ -CaF ₂ System in Preparation of Al-Ca Alloys by Fused Salt Electrolysis.....	77
<i>J. Li, W. Cao, M. Zhang, and Y. Wang</i>	
Recovery of Rare Earth Metals (REMs) from Primary and Secondary Resources: A Review	81
<i>V. Kumar, M. Jha, A. Kumari, R. Panda, J. Kumar, and J. Lee</i>	
Mutual Separation of Rare Earths Using Chemically Modified Chitosan Immobilized with Functional Groups of Chelating Agents	89
<i>K. Inoue and S. Alam</i>	
Electrochemistry for Nd Electrowinning from Fluoride-oxide Molten Salts	95
<i>B. Li, S. Liu, H. Wang, and Z. Zhao</i>	
Recovery of Rare Earth Metals from Wasted Magnet.....	99
<i>T. Nagai and T. Uzawa</i>	
Environment-Friendly Recycling Process for Rare Earth Metals in End-of-Life Electric Products.....	103
<i>T. Saeki, T. Akahori, Y. Miyamoto, M. Kyoj, M. Okamoto, T. Okabe, Y. Hiroshige, and T. Nemoto</i>	
Assessment of Environmental Impact of Rare Earth Metals Recycling from Used Magnets.....	107
<i>T. Akahori, Y. Hiroshige, M. Motoshita, H. Hatayama, and K. Tahara</i>	

Titanium, Lithium, Yttrium, and Zirconium

A Clean Titanium Sponge Production Process and New Method for the Recycling of Magnesium and Chlorine ...	115
<i>L. Niu, A. Zhou, T. Zhang, W. Wang, G. Lv, and X. Jiang</i>	
Chemical Characterization of Transition Metal (Nb, V, Zr) Impurities in Rutile.....	121
<i>T. Makanyire and A. Jha</i>	
Pre-oxidation and Hydrogen Reduction of Panzhihua Ilmenite Concentrate	127
<i>W. Xiao, X. Lu, W. Ding, C. Li, and X. Zou</i>	
Thermodynamic Properties of Different Titanium Ions in Fused LiCl-KCl Eutectic.....	133
<i>J. Song, Q. Wang, X. Zhu, J. Hou, S. Jiao, and H. Zhu</i>	
Silicon-thermic Reduction of Complex Lithium Aluminate under Vacuum	139
<i>Y. Di, X. Pan, J. Peng, Y. Wang, and N. Feng</i>	
Extraction of Yttrium from Ferruginous Sandstone, Southwestern Sinai, Egypt	143
<i>O. El Hussaini, H. Saalman, and M. Mahmoud</i>	
Sublimation Kinetics of Zirconium Tetrachloride (ZrCl ₄) for Producing Zr Sponge.....	149
<i>J. Shin, M. Choi, D. Min, and J. Park</i>	

Rhenium, Tin, Vanadium and SX Processing

Electrochemical Dissolution of Rhenium Bearing Super Alloys.....	157
<i>J. Hiskey and J. Snowberger III</i>	
Sodium Stannate Preparation from Cassiterite Concentrate and Sodium Carbonate by Roasting under a CO/CO ₂ Atmosphere.....	163
<i>Y. Zhang, Z. Su, Z. You, B. Liu, G. Yang, G. Li, and T. Jiang</i>	
Thermodynamics of Carbon in Fe-V-Ni-Mo Alloy Melts.....	171
<i>D. Kim, M. Paek, S. Won, T. Kim, and J. Pak</i>	
Dynamic Adsorption Behaviour of Aqueous Vanadium onto Anion Exchange Resin	175
<i>C. Li, H. Li, L. Wang, S. An, and B. Xie</i>	
Ultrasonic-assisted Alkaline Leaching of Vanadium from Stone Coal	183
<i>X. Liu, X. Chen, J. Li, and Z. Zhao</i>	
Sodium Roasting Thermodynamics of Chromium-containing Vanadium Slag and Its Application	189
<i>H. Fang, H. Li, X. Li, and B. Xie</i>	
Definition of the Process to Separate Light Rare Earths by Working with (2-Ethylexyl)-Mono(2-Ethylexyl) Ester Phosphoric Acid (P507) in a Mixer Settler Battery	197
<i>A. Blasi, C. Sposato, G. Devincenzis, P. Garzone, and M. Morgana</i>	
Comparison Among Different Extractants, AS (2-Ethylhexyl)-Mono (2-Ethylhexyl) Ester Phosphonic Acid (P507), Secondary-octyl Phenoxy Acetic Acid (CA-12) and Bis (2, 4, 4-Trimethylpentyl) Phosphinic Acid (CYANEX272), in the Separation of Heavy Rare Earths via Hydrometallurgical Processes	201
<i>C. Sposato, A. Blasi, G. Devincenzis, P. Garzone, and M. Morgana</i>	

Poster Session

Dysprosium Extraction Using Molten Salt Process.....	207
<i>A. Abbasalizadeh, L. Teng, and S. Seetharaman</i>	
Author Index.....	209
Subject Index	211

**Rare Metal
Technology**

**20
14**

**Metalloids and
Rare Extraction
Process**

ADSORPTIVE RECOVERY OF ANTIMONY (III, V) USING METAL-LOADED ORANGE JUICE RESIDUE

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Keywords: Antimony(III,V), Adsorption, Recovery, Metal-loaded gel, Orange waste

Abstract

Orange juice residue, a biomass waste, was saponified with calcium hydroxide to prepare an adsorption gel rich in pectic acid. The gel was subsequently loaded with high valence metal ions such as Zr(IV) and Fe(III) to improve the adsorption behavior towards anionic species such as antimonite (Sb(III)) and antimonate (Sb(V)). From the adsorption isotherm test, the maximum adsorption capacity of the Zr(IV)-loaded gel was evaluated as 0.94 and 1.19 mmol/g for Sb(III) and Sb(V), respectively, while that of the Fe(III)-loaded gel was 1.12 and 1.19 mmol/g for Sb(III) and Sb(V), respectively. The interference of coexisting anionic species such as chloride and sulfate on the adsorption of both Sb(III) and Sb(V) were found to be negligible. The adsorbed Sb(III) and Sb(V) was desorbed using an acidic solution along with the loaded metal ions, Zr(IV) and Fe(III). The desorbed Sb(III) and Sb(V) were selectively recovered as sulfide precipitates with the addition of sodium sulfide.

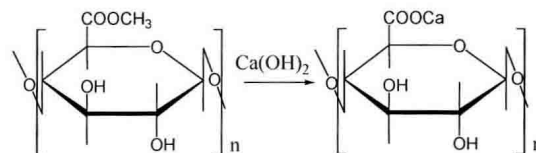
Introduction

Antimony, rare metal element, has seen extensive use in lead alloys, battery grids, bearing and power transmission equipment, ammunition, sheets and pipes. It also has found use in the production of semiconductors in the form of intermetallic compounds. Consequently, the significant environmental impact of mining antimony must be minimized through an effective and economic recovery method from various waste water or effluents containing low or trace concentrations of antimony. In addition, the presence of antimony in the environment has been a major concern due to its toxicity to many forms of life. It is well known that the most favored state in water is the pentavalent antimonate oxoanion, $\text{Sb}(\text{OH})_6^-$, while the other common inorganic form of antimony is antimonite, $\text{Sb}(\text{OH})_3$. A number of methods have been proposed and reported for the removal or recovery of antimony which include reduction and precipitation, solvent extraction, ion exchange and adsorption. Although adsorption of antimony has been studied by many authors, the adsorbents reported by these authors are expensive and time consuming. At this juncture, adsorption of antimony using agricultural by-products or biomass wastes has emerged as an option for the development of an economical, efficient and eco-friendly recovery method. It should be noted that selective separation of the oxo-anionic species of antimony as well as arsenic and phosphorus from other anionic species such as sulfate, chloride, etc. has proven difficult as such anionic species typically coexist in water in excess concentrations, thereby posing problematic for the well known Hoffmeister series of anion exchange. Therefore, for such cases it has been recommended to employ cation exchange materials such as commercially available cation exchange resins after loading with multi-valent cationic metal ions possessing a high affinity to the oxo-anionic species.

From such a viewpoint, the authors have developed an economical and environmentally benign adsorption gel from orange juice residue, an abundant agricultural by-product, obtained after the simple chemical treatment of saponification. In the juice factory, orange juice is produced by mechanically crushing whole orange; consequently, the residue contains both of outside thick peel skin and inside thin one. Orange juice residue has around 10 and several % pectin which is a carboxylated polysaccharide, in which pectic acid is partly esterified by the methyl group. It can be easily converted into pectic acid by saponification with alkaline materials such as calcium hydroxide. In our previous papers [1,2], the saponified orange juice residue, abbreviated as SOJR hereafter, was found to function as a natural cation exchanger as well as pure pectic acid. Consequently, metal loaded SOJR can be also expected to be employed as an adsorption gel for some anionic species [3-5]. In the present study, focus has been drawn toward assessing the potential of the aforementioned gel for the recovery of low concentrations of antimony from waste water by examining the effect of pH, sorption capacity, and influence of coexisting anions.

Experimental

The SOJR was prepared from crude orange juice residue kindly donated by JA Saga Beverage Co. Ltd., Japan, according to the saponification reaction shown in Scheme 1, the details of which are described in previous papers [1,3-5].



Scheme 1. Saponification of the methyl ester portion of orange pectin with lime water to produce SOJR.

The preparation of Fe(III)-loaded SOJR gel was carried out by exchanging Ca^{2+} ions in SOJR with Fe^{3+} ion as follows. Approximately 5 g of SOJR was equilibrated with 1000 ml of FeCl_3 solution for 24 h at a pH of 2.7 at 30°C. The suspension was then filtered and washed with deionized water until a neutral pH was obtained, followed by drying in an oven at 60°C for about 2 days to obtain the Fe(III)-loaded SOJR gel. Zr(IV)-loaded SOJR was prepared in a similar manner using ZrOCl_2 at a pH of 2.5. The loaded amounts of Fe(III) and Zr(IV) were evaluated as 1.87 and 1.40 mmol/g, respectively.

All adsorption tests were carried out batch-wise at 30 °C. The adsorption of Sb(III) and Sb(V) were carried out individually to examine the adsorption behavior of the metal-loaded SOJR gels towards antimony. Adsorption of antimony as a function of pH was first examined in a series of experiments where the initial

concentration of Sb(III) and Sb(V) were maintained constant (15 mg/l) at varying pH. Adsorption isotherms were examined by varying the concentration of antimony at the optimum pH thus determined. All batch adsorption experiments were carried out in 50 ml conical flasks by taking 25 mg (dry weight) of the gel together with 15 ml of the antimony solution. The flasks were then shaken in a thermostat equipped shaker (THOMAS thermostatic shaking incubator AT24R) maintained at 30°C and 140 rpm for approx. 24 h to attain equilibrium. After 24 h, the suspensions were filtered through a 1 μ m filter paper and their equilibrium concentrations were measured. The quantity of adsorbed Sb(III) and Sb(V) was calculated from the decrease in antimony concentration.

Batch-wise adsorption tests were carried out for the actual effluent generated in the production of polyester fiber which contained trace concentrations of antimony. This actual solution was kindly provided by Mitsuya Co. Ltd., Fukui, Japan.

The pH of all the sample solutions was measured using a DKK-TOA model HM-25G pH meter. The concentrations of antimony as well as other metal ions were measured using a Shimadzu model ICPS-8100 ICP/AES spectrometer.

Results and Discussion

Effect of pH

The plots of % adsorption of Sb(III) on Fe(III)- and Zr(IV)-loaded SOJR as well as that of % leakage of the loaded metal ions are shown at varying equilibrium pH in Fig 1. Quantitative adsorption of Sb(III) is observed over a wide pH range for both adsorbents; i.e. pH = 3–11 for Zr(IV)-loaded SOJR and 3–7 for Fe(III)-loaded SOJR. The decrease in the adsorption at high pH may be attributable to the anion exchange with hydroxyl ion as will be described later. The leakage of the loaded metal ions is negligible except for low pH range; i.e. it is observed at pH lower than 2 and 3 for Zr(IV)- and Fe(III)-loaded SOJR, respectively. The slight decrease in the adsorption of Sb(III) at pH lower than 3 may be attributable to the partial leakage of the loaded metal ions.

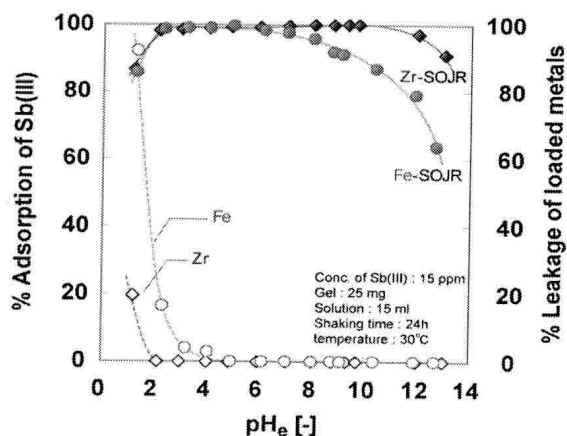


Figure 1. Effect of equilibrium pH on the adsorption of Sb(III) onto the Fe(III)- and Zr(IV)-loaded SOJR and on the leakage of the loaded metal ions.

Comparatively, the plots of % adsorption of Sb(V) on Fe(III)- and Zr(IV)-loaded SOJR is shown in Fig 2 as a function of equilibrium pH. In this case, the effect of pH appears more pronounced compared with the case of Sb(III).

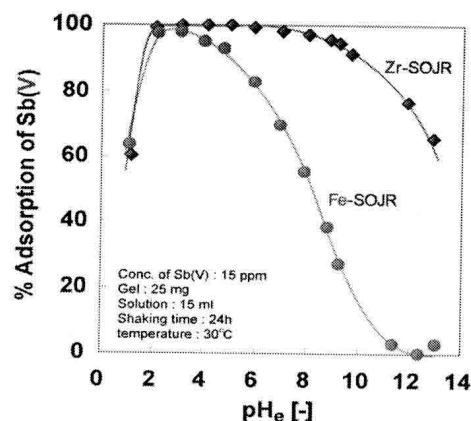


Figure 2. Effect of equilibrium pH on the adsorption of Sb(V) onto the Fe(III)- and Zr(IV)-loaded SOJR and on the leakage of the loaded metal ions.

Adsorption isotherms

The adsorption isotherms of both Sb(III) and Sb(V) were measured for each adsorbent as shown in Fig. 3 as plots of equilibrium concentration adsorbed, q , against the equilibrium solute concentration, C_e , at their optimum pH range observed in Figs.1 and 2 as stated in this figure. Evident from this figure is that the amount of adsorption increases with increasing equilibrium concentration within the low concentration range while it appears to tend to approach constant values corresponding to each species and adsorbent in the high concentration range as expected from the Langmuir's adsorption isotherm. Consequently, the observed adsorption isotherms were analyzed according to the Langmuir equation expressed by Eq.(1) to evaluate the adsorption parameters.

$$C_e/q = C_e/q_{\infty} + 1/(b q_{\infty}) \quad (1)$$

where C_e is the equilibrium concentration (mmol/l), q is the amount adsorbed at equilibrium (mmol/g), and q_{∞} and b are the maximum adsorption capacity (mmol/g) and adsorption equilibrium constant (l/mg), respectively.

The replots of the data shown in Fig.3 are illustrated in Figs. 4 and 5 for the adsorption on the Zr(IV)- and Fe(III)-loaded SOJR, respectively. In both figures, the plots appear to cluster on straight lines as expected from Eq.(1). From the slopes and intercepts with the ordinate of these straight lines, the values of the maximum adsorption capacities and adsorption equilibrium constants were evaluated, respectively, as listed in Table I.