Joint German-Mexican Research Programme for Sustainable Metallurgy – Report of the First Year

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The following article reports on the activities of the international project "Technical Feasibility and Legal Frame of Spent-Portable-Battery-Recycling in Mexico", a cooperation between IME Process Metallurgy and Metal Recycling, RWTH Aachen University and National Polytechnic Institute of Mexico (IPN). This program is organized by the Mexican High School of Chemical Engineering and Extractive Industries (ESIQIE) and funded by the DFG (German Research Association) and CONACYT (Mexican Council of Science and Technology). The first year of cooperation was determined by a joint workshop in Mexico City and experimental trials at IME in Aachen.

Keywords:

Battery recycling – Recycling – Bilateral research alliances – Arc furnace

Deutsch-Mexikanisches Forschungsprogramm für nachhaltige Metallurgie – Bericht über das erste Jahr

Der folgende Artikel beinhaltet die gemeinsamen Aktivitäten des Projektes" Technische Machbarkeit und rechtliche Rahmenbedingungen des Altbatterierecyclings in Mexico" des IME Metallurgische Prozesstechnik und Metallrecycling, RWTH Aachen University und dem Nationalen Polytechnischen Institut Mexico (IPN). Das Programm ist organisiert über die High School of Chemical Engineering and Extractive Industries (ESIQUIE) und wird finanziert durch die Deutsche Forschungsgemeinschaft und CONCAYT (Mexican Council of Science and Technology). Das erste Jahr dieser Kooperation wurde durch einen gemeinsamen Workshop in Mexico City und eine Versuchsreihe am IME in Aachen bestimmt.

Schlüsselwörter:

Batterierecycling – Recycling – Bilaterale Forschungsgemeinschaft – Lichtbogenofen

Programa de Investigación Conjunta entre México y Alemania para la Metalurgia Sostenible - Reporte del primer año

Programme de recherche conjoint germano-mexicain pour une gestion durable en métallurgie durable - rapport de la première année

1 Introduction

In 2008 the DFG and CONACYT issued a call for a joint German-Mexican project with the aim to support the formation of bilateral research alliances. Prof. Dr.-Ing. Bernd Friedrich initiated a project with his former student Dr. Ricardo Sanchez Alvarado, which includes a recycling conference in Mexico City and a joint experimental research program. The program includes visits of Aachen´s non-ferrous metallurgy team to Mexico and return visits of Mexican scientists at IME.

The German delegation, lead by Prof. Bernd Friedrich and five research assistants, travelled to Mexico in March 2010. In the first days, the delegation visited the Metallurgical Department of IPN and the Materials Research Centre at the UNAM (National Autonomic University of Mexico), one of the biggest Universities in the world with more than 300.000 students and the most important research institutions in Mexico. Prof. Friedrich presented RWTH Aachen University and the IME with an emphasis on the strong and successful cooperation between the academic world and industrial partners in the German research landscape and especially in Aachen.

Within the framework of the visit, a workshop entitled 1st Workshop on Battery-, Metals- and WEEE(electronic scrap)-Recycling, was held at the facilities of the National Polytechnic Institute of Mexico (IPN), with speakers of both partners and other Mexican experts. Around 150 participants, including students, academics and members from the Mexican government visited this venue.

The aim of this event was to promote the exchange of scientific and technological information between researchers and industry from Mexico and Germany and to identify further joined research projects. Presentations of recent results related to different areas of research and development in battery, electronic scrap and generally in non-ferrous recycling were presented, and opportunities for new areas of research and academic linkage to institutions of higher education, industry and research centres were discussed. From a Mexican academic point of view, it is important to stress, that investment in the education about recycling and promotion of the actualization of recycling-related laws is one of the most prominent topics for the future.

The event started with a welcome address from the Director of ESIQIE, M.Sc. Jesús Salvador Meza Espinoza and was supervised by the coordinators of the project from the Mexican side, Dr. José Federico Chávez Alcalá and Dr. Ricardo Gerardo Sánchez Alvarado. On the following pages, abstracts and summaries from the conference programme are presented.

2 Scientific programme

The scientific programme was opened by Prof. Friedrich who presented the research strategy of IME and highlighted potential areas for cooperation and student exchange opportunities with RWTH Aachen University. One of the topics was governmental assistance in the area of waste treatment, pollution control and recycling. After the presentation, possibilities of

studying and research abroad were discussed with the Mexican students who received information about technical facilities at IME, research areas, tendencies and current projects.

2.1 Hydrodynamic analysis of particles injected during lead refining

Eng. Victor H. Gutiérrez Perez, M.Sc. student, with co-authors *A. Cruz Ramírez, Elias Rangel Salinas, Ricardo G.S. Alvarado* and *M. Vargas Ramírez*, from the Instituto Politécnico Nacional (IPN) and the Centro de Investigación de Metalurgia y Materiales, UAEH, in Pachuca, Hgo.

Presented was the study of lead refining with the reactions and the hydrodynamics occuring during the injection of sulfur and zinc particles through a submerged lance into the lead bath with the aim to remove copper and silver. Mathematical modelling was developed with the software COMSOL v3.4 (Figure 1). The parameters considered were the crucible dimensions, injection influence and agitation effects for achieving the best performance of the lead refining process. Simulation results were validated with experimental data of residence times. Both results were compared obtaining a good similarity.

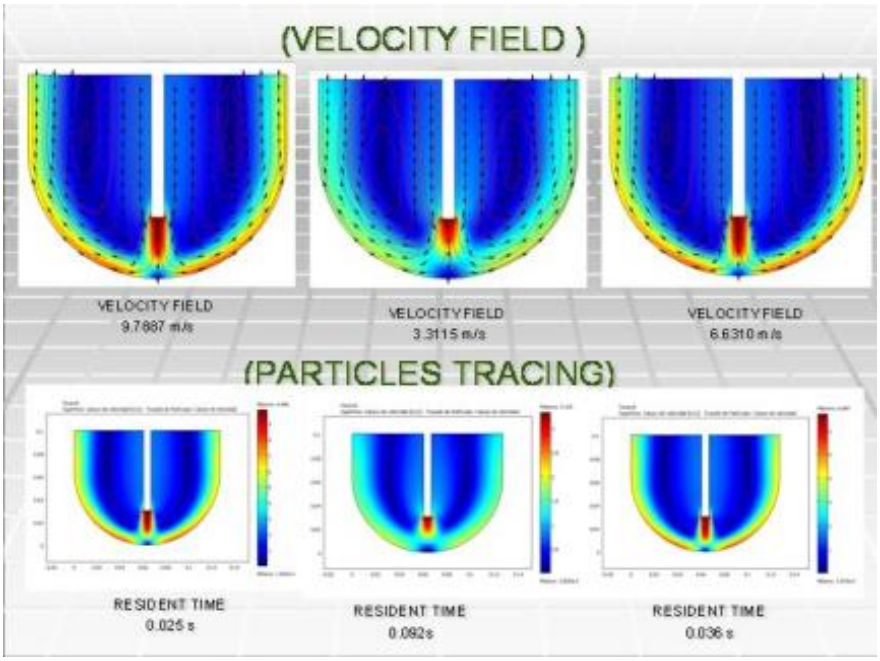

Fig. 1: Simulation of velocity fields and particle tracing of powder injection into a molten lead bath

2.2 Effect of MgO and CaO/SiO_2 on the immobilization of chromium in slags

Prof. Antonio Romero S. from ESIQIE and *Elda García R., Hugo Cabrera* and *Beatriz Zeifert*. This work investigated the chemical and mineralogical properties of CaO-SiO_2-Cr_2O_3-CaF_2-MgO slags, which were synthetically prepared for analyzing the effect of slag basicity (CaO/SiO_2) and MgO contents on the stability of the mineralogical species formed. The morphology and composition of the slags were analyzed by XRD and SEM-EDS, whilst their chemical stability was evaluated by leaching with an aqueous acetic acid solution. In slags with $CaO/SiO_2 = 1$, the main Cr-compound was found to be an $MgCr_2O_4$ spinel, which forms

octahedron crystals, followed by small amounts of $CaCr_2O_4$ and $CaCrO_4$. It was found that with increasing the slag basicity from 1 to 2 the compounds $MgCr_2O_4$ and $CaCr_2O_4$ were formed together with the Cr(V)-containing compound complex $Ca_5(CrO_4)_3F$ which forms hexagonal crystals. The results showed that the highest Cr concentration levels in the leaching liquors corresponded to slags with $CaO/SiO_2 = 2$, probably owing to the formation of $CaCrO_4$ and $Ca_5(CrO_4)_3F$ (Figure 2).

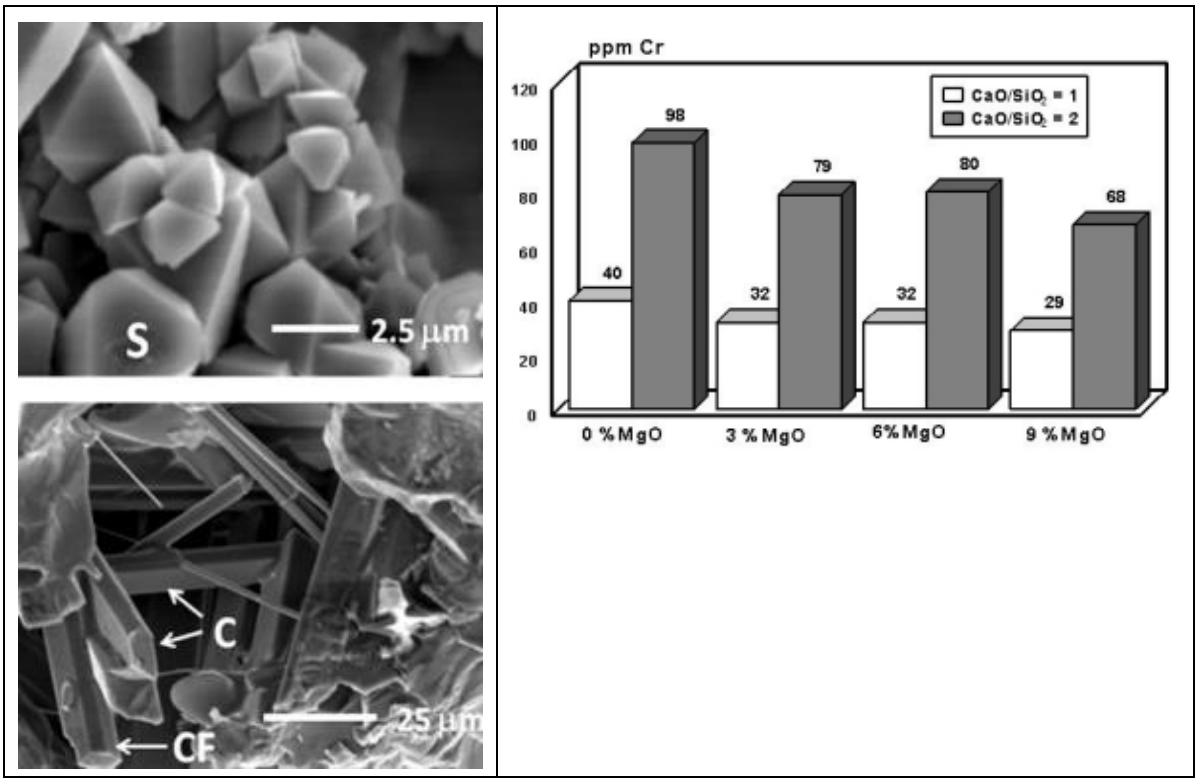

Fig. 2: SEM micrographs of the crystalline phases of the slag with 3 % MgO and $CaO/SiO_2 = 2$. CF: $Ca_5(CrO_4)_3F$. C: cuspidine ($Ca_4Si_2O_7F_2$). S: $MgCr_2O_4$ spinel (left side) and the effect of the CaO/SiO_2 ratio and MgO content on the leaching behaviour of Cr (right side).

2.3 Slags from copper industry – potential for improvements

Dipl.-Wirtsch.-Ing. Marco Zander (IME). Slags resulting from the pyrometallurgical process are an important by-product for the copper industry. The need for a "waste to product" treatment becomes obvious due to the significant larger volumes of slag compared to those of metal. At the IME, different procedures are developed to improve the metal recovery and to create a marketable mineral product from the original slag. The first treatment is improved slag cleaning directly in the SAF using coke injection. Its benefit in comparison to the traditional method is that it decreases the process duration by accelerated kinetics and improves the efficiency by an increased reduction potential. Furthermore, different fluxes/additives are investigated in order to decrease the viscosity and the melting point of the slag. By means of electrodynamic slag movement using magnetic field the settling behaviour

of the metal droplets is positively influenced as a third option. An efficient, reasonable and interleaving combination of these procedures will be tested in the new IME´s research recycling centre (IRRC, Figure 3) in future.

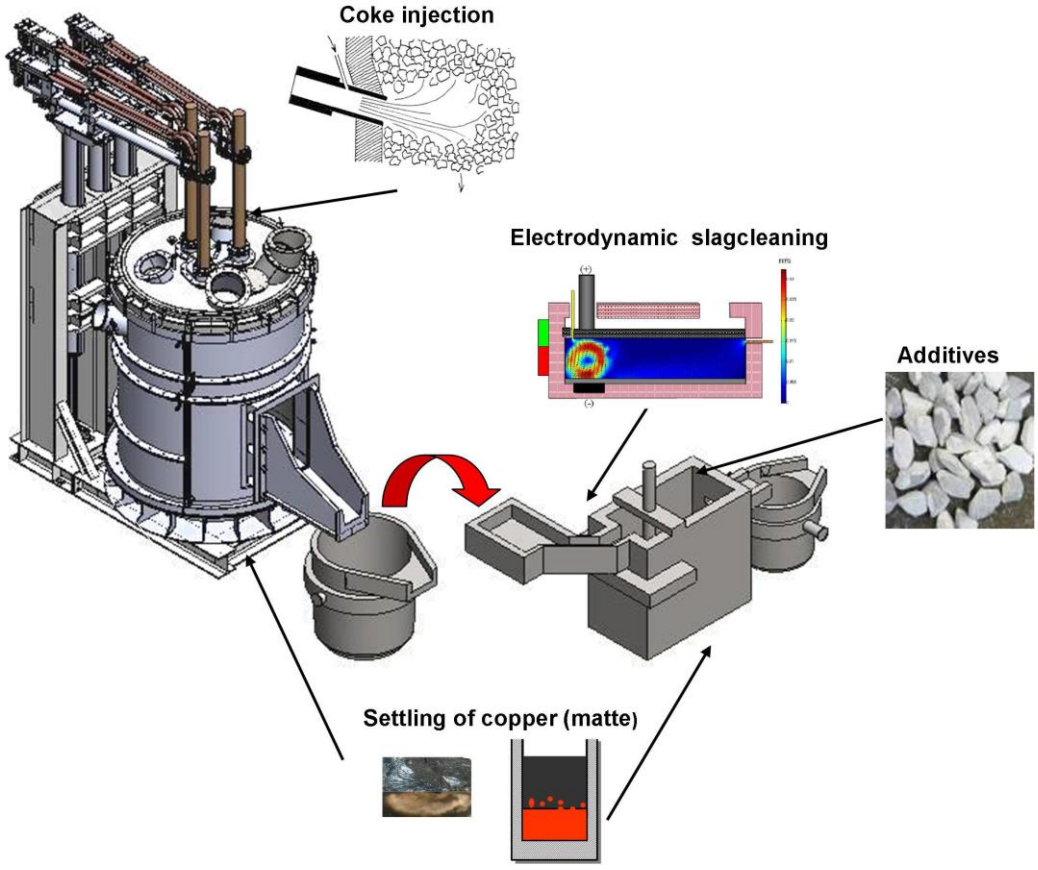

Fig. 3: Large-scale slag cleaning in the IRRC

2.4. Designing the slag layer in electric furnaces as splitting media for Li-ion battery scrap

Dipl.-Ing. Matthias Vest (IME). The IME, Institute for Process Metallurgy and Metal Recycling of the RWTH Aachen University, and its industrial partner ACCUREC Recycling GmbH are developing an integrated recycling process for Li-Ion automotive batteries, allowing fulfilling the EU recycling efficiency requirements of 50 wt.-%. After dissembling, vacuum-thermal treatment of discharged battery modules, mechanical treatment and separation, a fine fraction is gained, which contains most of the Li and all the Co, Ni and Mn content of a Li-ion battery. This fine fraction is agglomerated and treated in a pyrometallurgical SAF process (Figure 4). Co, Ni and Mn are reduced and collected with a metal alloy by high yields. So far the lithium input is split up more or less equally onto the flue dust and the slag phase. The projects goal is to design a slag to maximize the Li distribution towards the flue dust.

Figure 4: Lab-Scale battery recycling in an EAF at the IME

2.5 Myths and facts about batteries. The reality about batteries in Mexico

Ing. Tonatiuh García, Asociación Mexicana de Pilas (Batteries Mexican Association, BMA). The BMA runs an office for battery-recycling in Mexico with engineer Tonatiuh García being the actual president of the association. BMA collects information about portable and non-portable battery consumption for rechargeable and non rechargeable systems and also data on battery-waste generation in Mexico (Figure 5).

Mexican population reaches more than 100 million offering a large market for portable batteries that is dominated by the alkali-manganese system. According to statistics, in Mexico about six batteries per capita are annually consumed and since some years all of them are imported. However, the recycling is not very attractive for the Mexican industry. Some studies and projects have been done that are mainly focused on collecting strategies, sorting and processing technology, as well as treatment and landfill alternatives. Some of them even include life cycle analysis and end of life analysis. Eng. Tonatiuh García says that recycling and even production are not yet feasible in countries such as Mexico, because laws and politics are not appropriate for that. He says also that some recent studies showed that the landfill of waste batteries is probably the best option during this time.

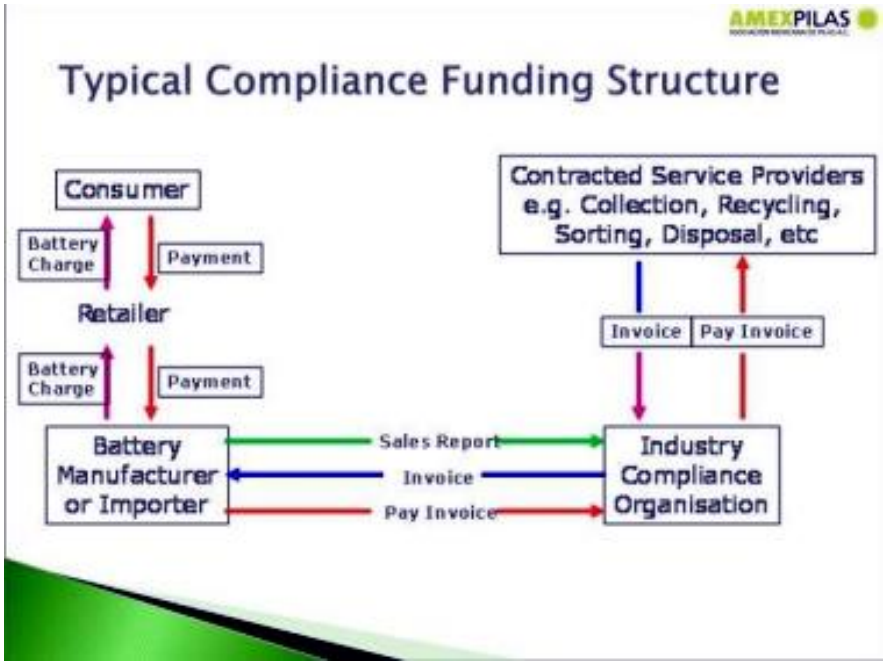

Fig. 5: Battery recycling in Mexico

2.6 Spent batteries to produce high value oxide materials

Dr. Elia Palacios Beas (IPN). The development of a hydrometallurgical procedure for obtaining Mn/Zn-spinel ferrites from spent batteries at a laboratory scale was presented. All the chemical reactions, from the elimination of Hg, selective leaching, precipitation of the precursor species with Fe, Mn and Zn and the calcination process at different temperatures and times are presented that lead to synthesis of high purity spinel-ferrites (Figure 6). By this method a valuable product can be produced from spent batteries.

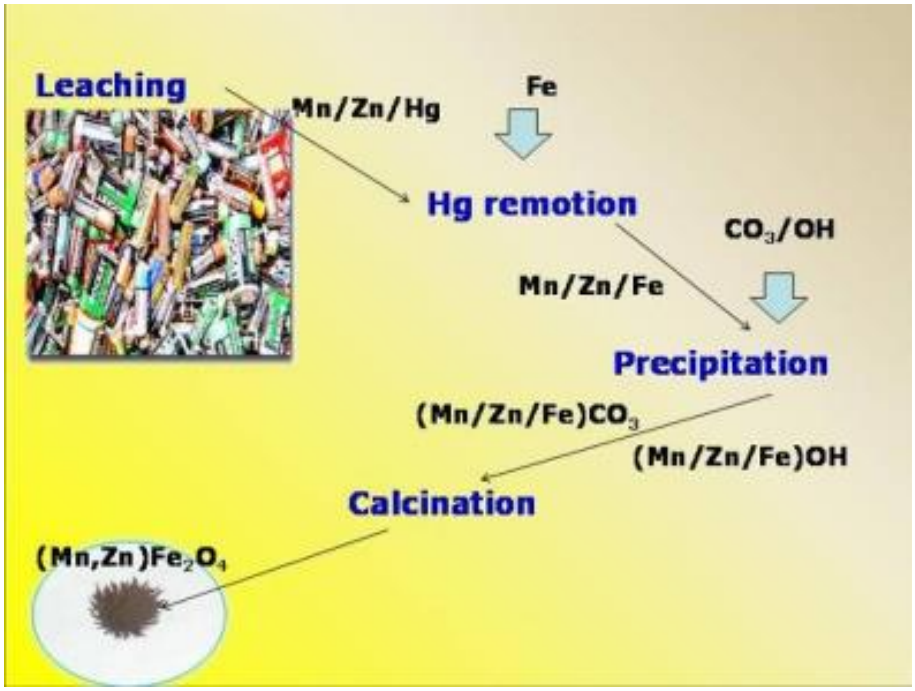

Fig. 6: Hydrometallurgical battery recycling by obtaining Mn/Zn ferrites

2.7 Submerged arc furnace technology – chances for recycling of silicon wafer scrap

Dipl.-Ing. Benjamin Jaroni (IME). Electric Arc Furnaces (EAF) can reach very high temperatures (> 2200 K) comparing to resistance or induction furnaces. In combination with the high availability, flexibility and a manageable investment Electric Arc Furnaces are qualified for a lot of different recycling processes. Pyrometallurgical recycling of silicon wafer production scrap is only one research project on the IME using EAF. To cover the hole line from lab scale to pilot scale the IME build up a new 1 MW EAF (Figure 7). This furnace can be used for 3-phase current or DC-processes, so it is possible to compare these main process types.

Figure 7: Recycling in SAF at the IME

2.8 Thermophysical properties measurement of molten phases

M.Sc. Semiramis Akbari (IME). The exact knowledge of thermophysical properties of molten phases is crucial to modern metallurgy. It leads to optimized process windows including better metal-slag separation, suitable slag selection or reduced slag-refractory wetting. The most important properties are melting and boiling points, electrical and thermal conductivity, melting and transition enthalpies, wetting angle, density, surface tension and viscosity. Here, the present opportunities, methods and uncertainties of characterization of molten phases with the focus on four properties (density, viscosity, surface tension and contact angle) were represented. The methodologies principles applied in this presentation are including buoyancy-flotation method for density, maximum bubble pressure method for surface tension (Figure 8), amplitude and damping methods for viscosity as well as sessile drop method for contact angle. Beside the complexity and the high accuracy of the methods, selection of the most appropriate materials for measuring devices are of big challenges as well, due to the high temperature and – very often – reactivity/corrosivity of the investigated molten phases (such as salts or slags).

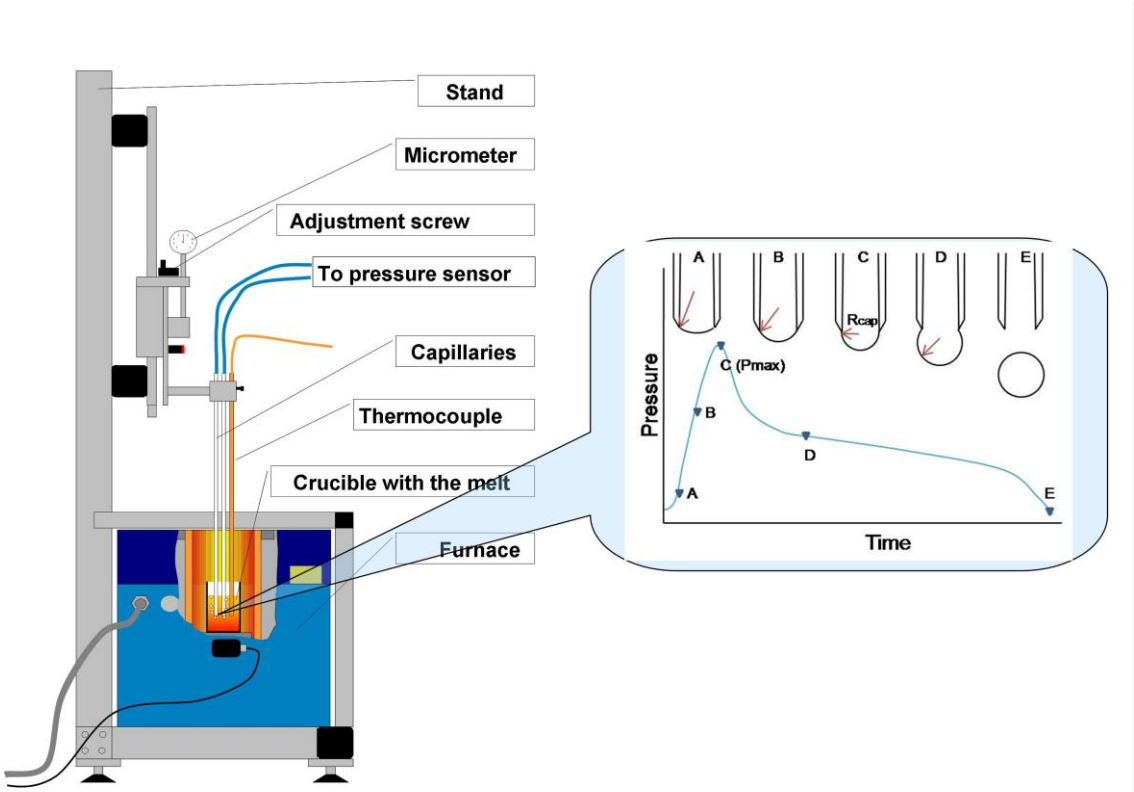

Fig. 8: Instrument and principle of surface tension measurement based on max. bubble pressure method

2.9 Electronic scrap recycling in Mexico

Private Consultant *Dr. Guillermo Román Moguel*. Although electronic waste becomes a very important issue, and there are international conventions for this, the possibilities and technology needed for recycling these wastes depend very much on infrastructure, local regulations and habits of the population. In all of these items, Mexico behaves differently than European countries, for example, technological appliances mostly still use CRT monitors and therefore contain lead. Analytical capabilities need to grow in Mexico for research and development. Already since 2006 estimations of electronic scrap in Mexico have been made by different methodologies (Figure 9). A first diagnosis/inventory is developed in this talk: 220,000 to 370,000 tons of electronic scrap has been estimated in 2009, but passive inventory has to be considered. Collection presents a major challenge. A management plan and public-private partnerships are suggested to address this issue.

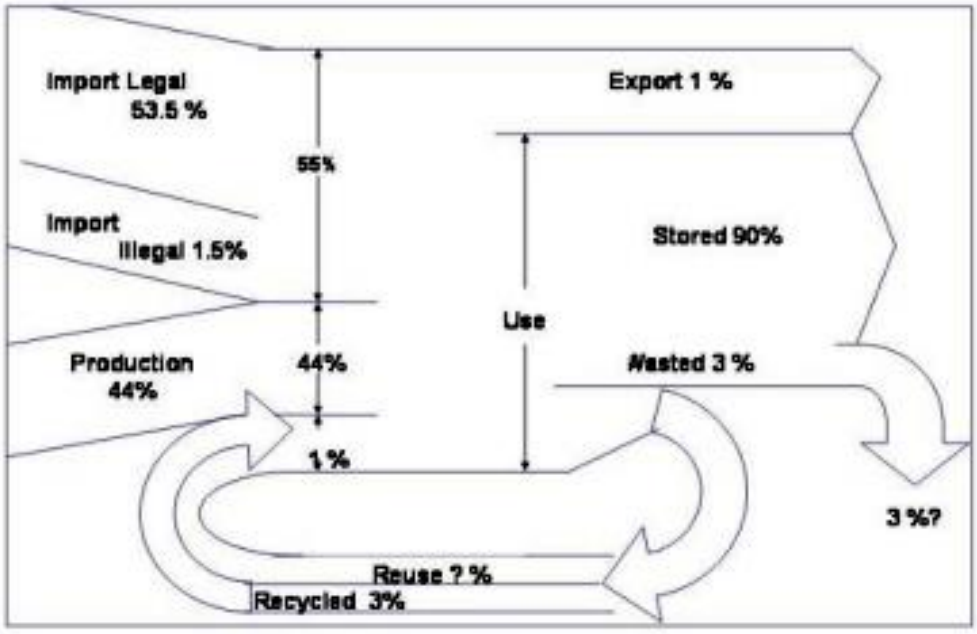

Fig. 9: Materials balance of electronic goods in México

2.10 TBRC slag bath smelting process for WEEE scraps

Dipl.-Ing. Sebastian Maurell-Lopez (IME). WEEE-scrap (Waste of Electrical and Electronic Equipment) is a very important secondary raw material. It contains a lot of valuable and strategically materials. After a brief introduction of what WEEE is specifically the state of the art with advantages and disadvantages of the WEEE recycling is presented. The new recycling concept of WEEE, which is developed at the IME, was explained. A part, the new TBRC (Figure 10) and the off-gas cleaning system, of the newly build IRRC (IME´s Recycling Research Centre) was shown.

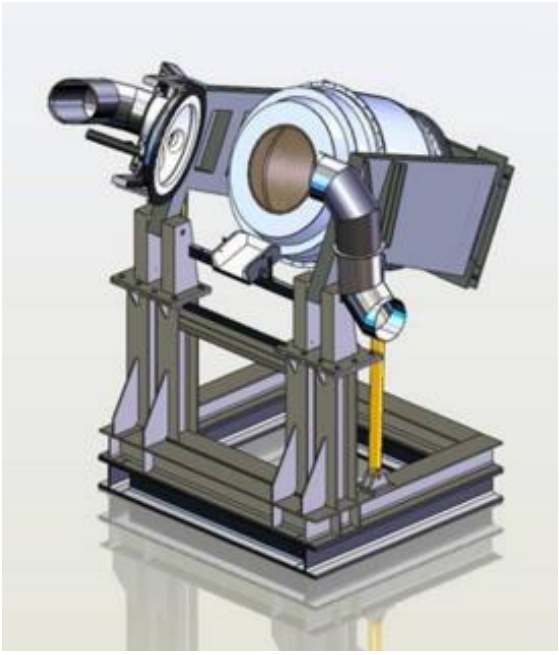

Fig. 10: Large scale TBRC for WEEE-scrap recycling

3 Impressions of the workshop week

The workshop was a great opportunity to discuss about present problems associated with recycling and related areas (Figure 11), but also to compare the reasons for different recycling levels in Mexico and the European Union. A first major result of the workshop is that, on the field of battery recycling, a new project concerning copper slag cleaning was initiated between the academic partners IME and IPN together with a Mexican company. The visit of the German research group included an interview with the academic authorities of IPN in order to set the basis for a cooperation contract that will allow the exchange of students and researchers, academic cooperation, technology transfer, etc.

The workshop participants visited Mexico City area and some of the most important sightseeing spots, including the oldest and biggest cathedral in Latin-America, a place called Tlatelolco, where is possible to experience the mixture of the Prehispanic, Spanish and modern culture in one spot. The 2000 year old Teotihuacán pyramids were also attended by the group during the weekend.

Fig. 11: Workshop impressions

4 First joint research activities

In November 2010 Dr. Chavez and Dr. R. Sanchez took chance for a two weeks research stay at IME, Aachen with the goal set-up the new joint project together with the Copper Company Mexicana Cobre (Figure 12). Available infrastructure (lab-scale furnaces) at IME was used for carrying out nine melting trials investigating the behaviour of the process slag provided by Minera. The aim of the trials was to improve copper extraction from the slag and to yield a saleable slag product. Because of the increase of copper price and more strict environmental regulations, slag treatment becomes a more and more important topic for the Mexican industry. Figure 13 shows the experimental setup of the lab-scale induction furnace trials at IME.

Figure 12: Research visit of the Mexican delegation at the IME

Figure 13: Lab-scale slag treatment trials

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