

AGRICOLA RESEARCH CENTRE: INTERACTIONS IN MULTI-COMPONENT MINERAL SYSTEMS (ARC-MMS)

Oleg N. Antzutkin¹, Hanumantha Rao¹, Fatai Ikumapai¹, Allan Holmgren¹, Lars Gunneriusson¹, Björn Johansson², Andreas Berggren², Anna-Carin Larsson¹, Sven Öberg³, Jonas Hedlund¹, Johanne Mouzon¹, Iftekhar Uddin Bhuiyan¹, Seija Forsmo⁴

Affiliations: ¹Division of Sustainable and Process Engineering, Department of Civil and Environmental and Natural Resources Engineering; ³Department of Mathematics, Luleå University of Technology; ²New Boliden AB; ⁴LKAB.

1. Goals of ARC-MMS

Understanding the interactions in multi-component mineral systems is of utmost importance for a deeper understanding of flotation, agglomeration and environmental sustainability. ARC-MMS has identified the following goals in three subprojects running from early 2008:

(i) To provide remedies to selectively regulate surface properties of zinc-copper-lead-iron sulfide minerals, which are affected by recycled process water. For these, understanding of the effects of major and minor ionic species, present in recycled process waters, on sulfide mineral flotation at New Boliden and Lundin Mining, are needed.

(ii) To explore the molecular scale approach in understanding of behaviour of dithiophosphate and xanthate collectors on surfaces of sulfide minerals and to utilize understanding of adsorption mechanisms of these collectors in improving selectivity and recovery of the valuable sulfide minerals.

(iii) To supply a new type of 3D data for water, air bubbles, flotation reagents and particles in wet iron ore pellets produced at LKAB and to create remedies for controlling of air-bubble inclusions in iron oxide pellets, which affect their mechanical strength and other properties important in metallurgy.

2. Methods

In the proposed programme Hallimond flotation, zeta-potential, XPS and FT-IR, potentiometric titrations, solid-state NMR spectroscopy and Density Functional Theory (DFT), electron microscopy and tomography are combined in an interactive and complementary fashion to extract information about interactions in multi-component mineral systems such as (i) complex zinc-copper-lead-iron sulfide minerals and (ii) iron

oxide pellets with fillers and binders. For morphological characterization of the latter systems, cryogenic scanning electron microscopy (cryo-SEM), image analysis of scanning electron micrographs and X-ray microtomography (XMT) were applied for the first time. In addition, microtomography with submicron resolution using synchrotron X-rays will be used for further high-resolution studies of the 3D microstructure in the pellets.

3. Results

A summary of results obtained in all three running subprojects of the programme are summarized below:

3.1 Recycling of process water and influence of its chemistry on sulfide flotation and flotation selectivity

Reference [1]: "Recycling of flotation effluents through the ore processing plant is one of the ways of reducing both plant-operating costs and industrial impact onto the local ecosystem. Such waters, named acid mine drainage (AMD), if discharged from sulfide flotation are gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) saturated and have a high salinity (on the order of 1000 ppm). As minor species, they commonly contain reduced sulfur compounds, RSC, such as SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_5^{2-}$, and $\text{S}_4\text{O}_6^{2-}$, cations of ferrous and non-ferrous metals, frothing molecules, residual chemical reagents and products of their degradation. Consequently, the key step towards developing scientific approaches of recycling of the tailing waters is elucidation of how and in what extent the tailing water components influence flotation of sulfides.

Hallimond flotation experiments indicated depression of chalcopyrite, galena and sphalerite and activation of pyrite in the presence of calcium and sulfate ions with potassium amyl xanthate as collector. Calcium ions have significant influence on zeta-potential characteristics and xanthate adsorption behavior of chalcopyrite, galena, sphalerite and pyrite compared to sulfate ions. FTIR and XPS studies revealed the presence of surface oxidized sulfoxyl species and surface iron and calcium carbonates on **chalcopyrite** in the presence of process water and water containing calcium ions, surface oxidized sulfoxyl and carbonate species on **galena** in the presence of deionized water, process water and water containing calcium and sulfate ions, hydrated surface oxidized species and surface iron and calcium carbonates on **pyrite** in the presence of process water and water containing calcium ions all at pH 10.5, in which the surface species influenced xanthate adsorption. The presence of surface oxidized sulfoxyl and carbonate species on **sphalerite** were also revealed at pH 11.5 in the presence of deionized water, process water and water containing calcium and sulfate ions, in which surface species do not influence xanthate adsorption."

3.2 Molecular scale approach towards behaviour of collectors on sulfide surfaces

Reference [2]: To explain the interactions of collectors with mineral surfaces in the course of froth flotation of sulfide minerals, ^{13}C and ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy was invoked in combination with Density Functional Theory (DFT) quantum mechanical calculations. Each specific type of interaction between a collector and a mineral surface has its own characteristic NMR signal. For signal assignment, model compounds were prepared and studied, both experimentally (by solid state NMR) and theoretically (by DFT calculations): The ^{13}C NMR chemical shifts and chemical shift anisotropies of potassium *iso*-propylxanthate (KX) and six of its decomposition products (see selected examples in Fig. 1a), which are known to be formed during flotation, were identified. The agreement between experimental and calculated NMR parameters was found excellent [2]. When adsorbed on a mineral surface, the electronic environment around the xanthate CS_2 -group, and thus all NMR parameters, do change. Calculations on related lead(II) compounds (see Fig. 1b) were also performed and these results will be invoked in identification of the surface adsorbed species on PbS. From NMR experimental data on surface adsorption of xanthates on PbS and ZnS activated by Pb^{2+} and Cu^{2+} it is suggested that xanthates are decomposing through several steps depending on the length of alkyl substitutes and that the behaviour of the xanthates is different, when adsorbed on PbS, on lead-activated ZnS and on copper-activated ZnS, respectively.

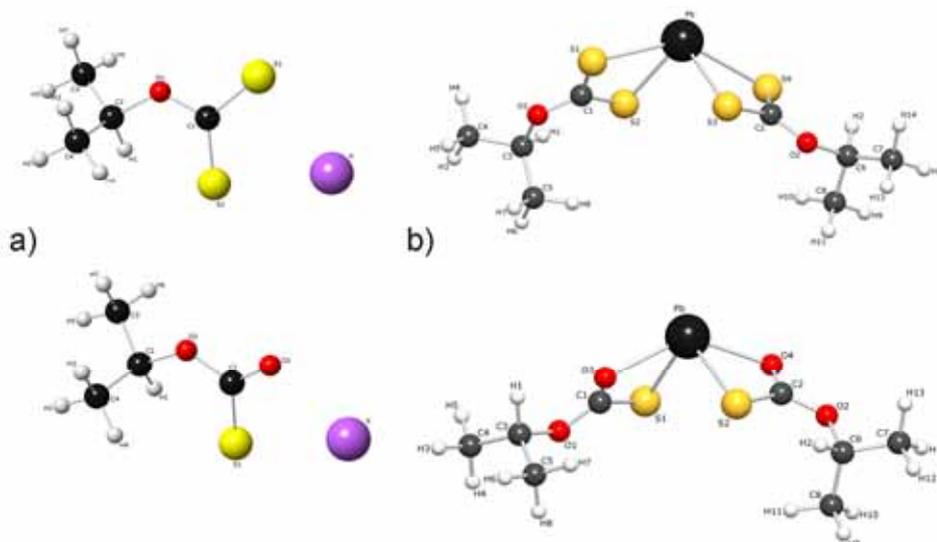


Figure 1. Potassium *iso*-propylxanthate and one of its decomposition products (monothiocarbonate, MTC) (a); Lead(II) *iso*-propylxanthate and lead(II) *iso*-propyl-MTC complexes (b). Color code: H (white), C (gray), O (red), S (yellow), K (pink) and Pb (black).

3.3 Three-dimensional (3D) data for iron ore pellets

Reference [3]: “A novel methodology for cryogenic scanning electron microscopy (cryo-SEM), image analysis (IA) of SEM micrographs and X-ray microtomography (XMT) was developed for obtaining important information on the morphology of wet iron ore pellets. Cryo-SEM and freeze fracturing was used to observe entrapped air bubbles and the arrangement of particles around bubbles and in the matrix of wet green pellets. The observations of samples prepared by plunge and unidirectional freezing indicate that unidirectional freezing facilitates the observation of entrapped bubbles with minimum formation of artifacts, whereas plunge freezing enables observation of the degree of water filling at the outer surface of wet pellets with minimum amount of artifacts. It was also observed in the wet pellets that the size of water domains in the matrix is quite small and the finer grains are mixed with coarser grains resulting in a denser matrix, whereas no fine grains were observed in the vicinity of air bubbles. Two types of pellets prepared with and without addition of extra flotation reagent prior to balling were studied using IA and XMT. IA of scanning electron micrographs of epoxy-impregnated pellets was used to separate bubble porosity from packing porosity and to quantify the former. The individual SEM micrographs acquired by a backscattered electron detector were reconstructed to provide the entire two-dimensional (2D) sections of the pellets. The 2D data obtained by IA were unfolded to three-dimensional (3D) by stereology and relatively good agreement with XMT data was observed. The size and amount of air bubbles could be quantified with both techniques. The addition of extra flotation reagent was found to increase the number of entrapped air bubbles and slightly decrease the median bubble diameter. The additional entrapped air bubbles due to the addition of extra flotation reagent was shown to be responsible for the difference in total porosity observed by mercury porosimetry between the two types of pellets.”

4. Partners of ARC-MMS and International Collaboration

ARC-MMS programme with a total budget of 13.52 Mkr (2008-2012) is financed by VINNOVA's *Strategic Mining Research Programme* (50%) and co-financed by the Swedish leading mining companies and LTU. The following partners are involved in this programme:

Luleå University of Technology: lead partner, which carries out all lab testing, spectroscopy, quantum-mechanical calculations, microscopy and tomography.

New Boliden AB: one of the core industrial partners, which co-finances all three subprojects (20.7%) and assists in sampling of process waters at flotation pulps and in the elemental analysis of samples.

LKAB: one of the core industrial partners, which co-finances subproject 3 (18.5%) and assists in production and testing of iron-oxide pellets (at R&D laboratory in Gällivare) before SEM and TEM tomography studies on the same pellets at LTU.

Lundin Mining: has provided financial support for the first 18 months in subprojects 1 and 2 (6.8%). However, the company has terminated its participation in ARC-MMS from

September 2009, because of the economical crisis. Most of company's activities have been already moved from Sweden to Canada.

ARC-MMS has a fruitful collaboration with Kola Research Center (Russia), LaTrobe University, Bendigo (Australia), Ian Wark Research Institute, University of South Australia, and Research Institute of Natural Resources, Blagoveshchensk (Russia).

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