Environmental Aspects of Metals Removal from Waters and Gold Recovery

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Mining and metals processing are not invisible activities and are heavy industries, which require energy, water, chemicals, and land area. Recently more emphasis is given to environmental and societal aspects in mining and processing. Development of good practices with improved resource efficiency, new recovery methods and sustainability thinking are increasingly required. This work shows pH titration method for acid mine drainage (AMD) water incorporated with aqueous thermodynamic model for selective metals precipitation from complex solution. Also two examples on gold recovery methods from aqueous streams are shown: biosorption using fungal matter and solvent extraction using a task-specific ionic liquid. By understanding chemical thermodynamics and natural phenomena, there is a better chance of developing solutions for environmental problems and new industrial processes. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2739–2748, 2015

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Introduction

Minerals, metals, and their processed high-end complex materials exist in our daily lives including infrastructure, vehicles, appliances, and electronic products. All these contain either mined metals and partly recycled metals and materials.

The global mineral market, driven primarily by the growing standard of living and urbanization of industrial and development countries, is expected to lead to a mineral resource gap in future years unless new mineral sources and more efficient technologies are developed. In addition to more efficient extraction processes, the expected resource gap requires more careful use of mineral raw materials over a wide range of products. Also the concentrations of metals found in primary deposits are now lower than that found before and furthermore the deposits are more complex than before. These trends lead to a need to develop new innovative technologies for economically sustainable extraction and recovery of metals.

Also a proper management of the socioenvironmental impacts, that is, dealing of the wastes related to general mineral extraction processes, is vital for successful operations.

Within the European Union (EU), critical raw material usage is expected to increase due to green technologies, electric vehicles, special bulk applications for materials such as steel, and the increased need for materials which can withstand extreme conditions.[1] To tackle this challenge, for example, European Union is focusing its activities in the raw material sector on plans that include the raw materials initiative and a strategy implementation plan on raw materials by European Innovation Partnership.[2,3]

There is a clear need for tools and methods that allow for more rigorous and sustainable mining, processing, and material design. Mining waste and tailings as well as metallurgical waste and industrial waste-streams combined with anthropogenic waste streams are potential sources of raw materials. Material preparation in these areas is challenging because of the complex mixed chemistries, impurities, and mineral structures, and these have a direct effect on the economics, energy consumption, chemical consumption, and resultant wastewater issues.

The amount of mining waste worldwide, that involves flotation underflow, leaching residues, side rock, and precipitates is huge and is expected to increase. The average copper ore grades, for instance, has during the recent decades dropped to below 1.0%, and this has a direct link to increasing amounts of mining waste.[4]

Primary production and mining are the main producers of industrial waste. In Finland, about 55 Mt of waste is generated annually by the mining industry (this amounts to 53% of the total industrial waste of 104 Mt).[5] This mining waste amount is increasing annually and can result in significant and sometimes irreversible degradation to ecosystems.[6]

The problem with waste rock is that the content of metals are typically uneconomically low for processing but in the long term can generate environmentally harmful metal rich solutions, for example, due to acid formation through sulphide oxidation.[7] Major mine tailings sites, mineralogies, and major trace metals in Europe, for example, have recently been identified.[8]

Waste mineral (rock) typically contains not only base metals, iron, aluminum, silicon, and so forth but also both traces of valuable metals together with hazardous substances such as arsenic, chromium, lead, and other metals which can cause environmental problems. One of these serious environmental

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problems is acid mine drainage (AMD).[9,10] The problem exists in operating mines as well as in closed mines. The correct mining closure handling and maintenance procedure is crucial for the environment.

There can be seen increasing conflict between the growing amounts of waste, which includes mining waste and hazardous waste, and the simultaneous societal need to improve resource efficiency, which includes, recycling, improved recoveries of metals in a cost effective manner, and reduced dependency of foreign imports. The demand for improved treatment methods in the mining and extraction industry is increasing due to better public awareness. Unfortunately, mining processes have not yet been developed to the level where there is no environmental impact. This is a global problem which must be dealt with. There is a growing demand and political will for closed loop production and toward zero waste society. This creates need to improve methods and processes for utilization of waste, side-streams, and tailings in the whole chain. Mining and refining industry has a need to respond to social interest of less hazardous waste and simultaneously need for economical use of raw materials. An example of governmental concern covering technological and societal aspects of mining, is the action plan implemented by the Finnish government on sustainable mining.[11] Their brief includes a social licence for operating existing mines as well as opening new ones.

The requirements of process water are highly dependent on specific industrial applications. Every mine site is specific in terms of ore type, gangue material, plant situation, water quality, and so forth. Water quality may have significant impact on the performance of the separate unit processes and the whole process chain. Therefore, water recycling and reuse needs to be assessed individually, case-by-case.

Acid Mine Drainage

Mining can have a strong and long-standing impact on the environment. The environmental effects from old mining activities on the surroundings can easily be observed in many mineral rich regions of our globe. The detrimental impacts may encompass any or all of the following: contaminated groundwater and soil due to acidic drainage; dust arising from blasting and quarrying; change in the landscape and ecosystem due to the mining operation. It has been a long-term pursuit, for example, within the European Union to gather data of the status of mining sites to develop legislation and guidance for improved environmental sustainability for mining, quarrying and ore-processing operations, including their waste disposal.[12] A particular focus is laid on limiting the risk of pollution caused by wash waters and AMD, which could lead to leakage of pollutants into the groundwater. As for water contamination, mining of sulfide ores such as pyrite, pyrrhotite, and chalcopyrite poses the greatest dangers. When these minerals and gangue thereof are exposed to oxidative conditions in aqueous solutions, the oxidation sequence will lead to AMD which will potentially leach metals from the surroundings and contaminate the groundwater and soil. The polluted water can spread to large areas and have environmental impact over long distances.[13] Modern environmental legislation regulates discharges in an attempt to minimize environmental hazards.[14] The mining industry, therefore, faces increasing challenges to find sustainable practices for their wash waters and to deal with acid drainage. Water treatment methods and technologies are becoming an essential part of any mining activity.

Mine water is an aqueous stream containing various metal ions depending on the mineral deposit, that is, sulphide or oxide metallic ores, industrial minerals, or natural stones. Metallic ores exhibit the greatest threat as they often contain hazardous components, for example, arsenic, cadmium, chromium, mercury, nickel, lead, chloride, and cyanide.[15] Typically, the analysis of these waters shows some major metal cations and a larger number of metals in minor concentrations. As the sulphide ores often include the base metal as a “host” or “carrier,” they most often bear other metals as accompanying metalliferous components. Consequently, the list of trace metals appearing in the acid solution can be long, yet quite ore-specific, which requires different approaches for both monitoring and controlling the waters at each site.

Wastewaters from mines, especially sulphide ore mines, are usually acidic. Neutralization by lime or coal fly ash is, in fact, a well-known method to neutralize acid mine waters.[16] In lime neutralization, metals such as Fe, Zn, Cu, Al, and Pb are precipitated as hydroxides and a sludge composed of a mixture of gypsum and metal hydroxides is formed.[17] The product formed in traditional lime treatment is usually difficult to use due to the precipitation of mixed compounds. If a cost effective water treatment method that selectively precipitates compounds is developed, it would allow the utilization of the metals in large wastewater streams. For example, techniques such as the recovery of magnetite by selective precipitation and subsequent reductive precipitation are desired.[18] In biological treatments, sulfur-reducing bacteria generate H_2S, which subsequently causes the precipitation of metals as sulfides.[19] This novel approach has been subject to extensive research during the last few years.[20]

Most metal ions form specific stoichiometric compounds once the pH of the solution exceeds a compound-specific threshold, making it possible to selectively separate metals by controlling the pH. The concentrations of individual metal ions are relatively low, but the volumes of water are large, making process like precipitation a reasonable process alternative. Titration is a conventional and straightforward method to investigate the base neutralization capacity of AMD waters. Combined with multicomponent speciation models the titration curves may also be used to support a more detailed understanding of each drainage source and its pH buffering properties.[21] As stressed in the early work, titration curves serve as an inexpensive and valuable tool for determining the base neutralization capacity for acid mine waters. In this work, the titration curves were interpreted by employing an easy-to-use thermodynamic multiphase model in order to develop more advanced fractionation techniques for specified metals recovery. For this purpose, a modified method for base titration is proposed. Both the development and its commercial utilization for separating the metals of interest are supported by the multicomponent Gibbs energy minimization technique.

The highly acidic extremely metal rich AMD investigated here needs to be neutralized before discharge. A cost effective water treatment method that selectively precipitates metalliferous compounds would allow the utilization of the metals in these large wastewater streams and may thus become an additional source of revenue. Through collaboration between modelling and experimental work, a base titration procedure was developed to selectively separate metals in a sample AMD from the Pyhäsalmi Mine, Finland. Apart from copper and zinc, the selective separation titration would also allow the recovery of, for example, Fe and Al. Compared to neutralizing the acid, the recovery of copper and zinc comes at a relatively small additional expense. Filtering away the precipitates at specific pH-thresholds serves a dual purpose. It improves selectivity of metal recovery and reduces the modelling effort required to computationally reproduce the experiments. The experimental results were in excellent agreement with the model computations. This study is an example of benefits arising when modelling is performed concurrently with experimental efforts.

Experimental Analytical Recovery of Metals from Mine Water

Pyhäsalmi Mine is an underground pyrite, rich copper and zinc mine located in central Finland. In order to decide which acidic waste water to use in our experiments, the mining company provided the results from analyses (pH, conductivity, sulphate, copper, zinc, iron, and manganese) of many of their reservoirs. The reservoir with the largest amounts of copper and zinc was chosen for this work.

The composition of the chosen mine water sample was analyzed by inductively coupled plasma atomic emission spectroscopy (inductively coupled plasma atomic emission spectroscopy (ICP-AES), Thermo Jarrell Ash Iris Advantage by Thermo Jarrell Ash). Potassium was analyzed with flame atomic absorption spectroscopy (FAAS, Perkin Elmer Atomic Absorption Spectrometer Analyst 800 by Perkin Elmer).

The mine water from Pyhäsalmi contained a variety of dissolved metal cations. The major anion was sulphate and the pH was around 2. Therefore, the water mixture is best described as sulfuric acid with impurities. When base is added to this solution, the equilibrium pH increases monotonically, but far from linearly. The shape of the resulting titration curve depends largely on the amount and type of cations in the solution. The rough shape is a smoothed staircase, where every other segment represents a buffer-like region. In such a region, the equilibrium pH changes very little or not at all despite the addition of base. As the hydroxide ion concentration increases, complexes are formed with the metal ions. When the concentration of a complex exceeds its threshold, nucleation begins. Any further addition of base is spent on making a precipitate instead of raising the pH. The identity of the precipitate depends on thermodynamic potentials and prevailing kinetic conditions. The purity of a forming solid is determined by the rate of precipitation and the availability of suitable neutral molecules or ions in the solution. A fast reaction tends to trap other ions and molecules within the solid. A slower precipitation reaction allows the formation of more complex stoichiometric phases. Amphoteric precipitates dissolve once the hydroxide ion concentration increases enough. It is, therefore, necessary to remove the precipitates at specific intervals to enable selective recovery.

A typical titration analysis was performed by adding freshly opened 0.5 M sodium hydroxide into a 500 mL mine water sample using a computer controlled pH titration apparatus (799 GPT Titrino from Metrohm, Herisau, Switzerland). Dynamic equivalent point titration was used. The fresh AMD water sample was filtered by vacuum filtration using 0.45-μm pore size Supor® membrane disc filters (Pall Corporation) prior to use and after each chosen pH segment. The recovered solid fractions were analyzed by X-ray Diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM), and stereomicroscope. Optimal pH values for collecting the precipitates were chosen based on a preliminary titration experiments from which the computational model was developed and verified. Precipitations were collected at approximate pH values 3.6, 5, 8, 10, and 11. Although precipitates have been collected in several titration studies during titration,[22,23] the selection of recovery points undesirably allowed precipitates, especially amphoteric Al and Fe precipitates, the chance to dissolve back into the solution or undergo further modification. The model predicted that CO_2 (dissolved from atmosphere) affects the titration curve at high pH. Similar experimental findings are known.[21] Therefore, additional experiments were conducted with a steady stream of nitrogen gas bubbling through the liquid.

Thermochemical Modelling of Metal Precipitation from AMD Water

The proposed process was modelled using ChemSheet[24–26] for thermodynamic modelling of chemically reactive systems including hydrometallurgical separation of metals from water. The software is a thermodynamically rigorous computation platform based on the minimization of the Gibbs energy of multiphase and multicomponent systems. Similar mathematical constructs have previously been used successfully.[27–29] With appropriate data, ChemSheet models can be used to simulate reactors and processes in all fields of thermochemistry and tested in aqueous process solutions as well as in high temperature metallurgical systems. In multiphase thermochemistry, the “research programs” themselves may be customized and appear with their highly specialized databanks. The thermochemical data will then include the necessary interaction models for the complex phase mixtures, which appear as application specific, for example, different high-temperature operations in metallurgy. To ensure the usage of such data in process simulation software, various interfaces have been developed.[30–33]

ChemSheet, when introduced in 1999, was one of the software pioneers serving the need of coupling rigorous thermochemical software with more common, easy-to-use interfaces.[34]

ChemSheet provides an MS-Excel add-in coupling to the well-known ChemApp Gibbs energy solving program.[32] Also with ChemSheet, the unique Constrained Gibbs free energy method can be used to include dynamic constraints and reaction rates of kinetically restricted reactions, yet retaining full consistency of the multiphase thermodynamic model.[35,36] Within the model, electroneutrality conditions and elemental balances are always valid. In the model, the advancement of the chemical reaction is related to the chemical affinity defined by De Donder and to the corresponding Gibbs energy change. For reliable modelling, some experimental information or kinetic model and so forth is required to fix one or several system components like pH, partial pressure, temperature, or chemical amount. The multicomponent model will calculate the respective Gibbs energy minimum of the system showing the activities of the rest of the system components. For relative slow aqueous processes, this method has been used successfully for process development in pulp and paper industry and in metallurgical industry.[36] Figure 1 depicts the Excel spreadsheet connection to ChemApp in ChemSheet.

A multicomponent multiphase thermochemical model was constructed from thermodynamic data, atom balances, and select kinetic information. The model system contained Al^{3+}, Ba^{2+}, CO_3^{2-}, HCO_3^-, Ca^{2+}, Cl^-, Cu^{2+}, Fe^{3+}, H^+, K^+, Mg^{2+}, Mn^{2+}, Na^+, OH^-, SO_4^{2-}, HSO_4^-, and Zn^{2+} aqueous species. The aqueous solution was modelled by Pitzer equation. The

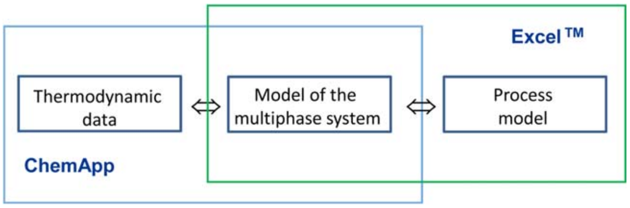

Figure 1. ChemSheet coupling of Gibbsian thermodynamics and spreadsheet calculations.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermodynamic parameters were gathered from the VTT Solution Database. The data for the three forms of solid zinc hydroxide were taken from FactSage.[37] After elimination of superfluous compounds, the revised model contained a gas phase with four constituents, an aqueous phase with 86 constituents, and 64 solid phases. $Fe(OH)_3$ was chosen as a proxy for hydrous ferric oxides such as goethite, ferrihydrite, and schwertmannite.[27] Any schwertmannite precipitated would eventually evolve into goethite, but the process takes time.[38]

Fresh mine water from the Pyhäsalmi pyrite rich copper and zinc mine had a pH around 2.4. According to the model, $Al_2(SO_4)_3$ and $Fe(OH)_3$ would precipitate spontaneously at this pH. This prediction is consistent with the discovery that small amounts of rusty orange or white precipitates formed during extended storage periods. Since the solid particles in the mine water samples were removed just prior to each titration experiment and the rate of precipitation was very low, these solids were suppressed during simulations. Because some of the experiments were performed in air, CO_2 absorption occurred during titration at high pH. However, it did generally not reach equilibrium, so the amount of CO_2 in the model was left as an adjustable parameter. The initial composition of the mine drainage water from Pyhäsalmi Mine is reported in Table 1. The uncertainties represent standard error (95% confidence interval) and the analyst's expert opinion based on peak shape (interference) and reproducibility (replicas). This liquid is classified as a highly acidic, extremely metal rich AMD.[39] The pH is close to the classification boundary (pH 3). Following the selection criteria of metals, only Cu, Zn, Fe, Cd, and Co are counted when determining metal richness.[39]

Table 1. Composition of the Chosen AMD Sample from Mine Water

	C (mg L^{-1})
Cu	14
Zn	350
Fe	850
Mn	43
Cd	0.27
K	3.5
Ca	500
Al	450
Mg	1120
Na	160
Co	0.40
S	10367
Conductivity	738 mS/m
pH	2.7

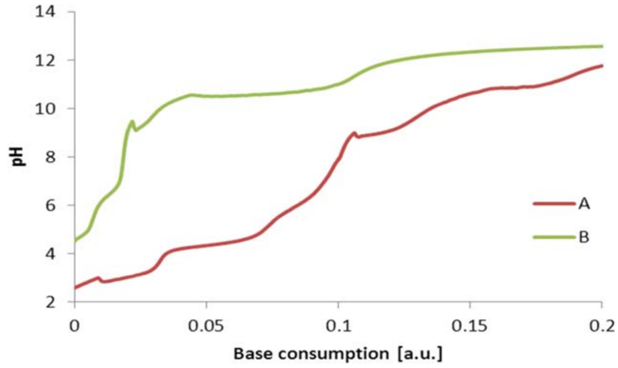

Figure 2. Continuous titration curves for AMD from Pyhäsalmi Mine.

Curve A (lower curve) was measured in air for the entire mixture. Curve B (upper curve) is for a solution with most of the iron and aluminum removed by pH induced precipitation. The liquid volume and the strength of the base were different in the two experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A neutralization method called Scheil-titration for AMD water was developed in order to characterize the precipitates and used as an example system for the aqueous thermodynamic model developed. Scheil theory and methodology have been used in physical metallurgy for long time.[40,41] In this method, applied in this work, the precipitated phases are removed from the solution as they appear. When each main phase is removed, they will not interact with the next appearing phase.

- In Scheil titration, the forming precipitates are removed before they react further. This is equivalent to filtering the precipitates away at specific pH thresholds.
- Removal of phase, as it appears, will supress the diffusion that would otherwise appear in the solid phase. This also prevents the solids from forming surface complexes.
- The pH values at which solids are removed are measured.
- The model yields the predictive composition of the solid phases, yields and aqueous phase composition. Also, the amount of neutralizing agent is estimated.

The major cations in the AMD solution are Mg and Fe. Also Zn, Ca, and Al were present in smaller, but still notable amounts. Representative experimental titration curves are shown in Figure 2. Curve A was measured for freshly filtered AMD. Curve B is for a solution with most of the iron and aluminum removed prior by pH induced precipitation. The titrations were carried out in ambient atmosphere.

The sudden drops in pH around 2.9 and 8.9 are due to large changes in ionic strength induced by massive precipitation. The titration curves show optimal precipitation recovery points around pH 3.6, 4.9, 7.4, 8.1, 9.4, and 11.1. The computational model was developed and refined to simulate the titration process. According to the simulations, the presence of carbon dioxide affects the precipitation of zinc, manganese, magnesium, and calcium. The major difference is the order and identity of Mn and Mg precipitates.

Figure 3 shows the order, identity, and magnitude of precipitates formed during titration according to the simulation. The modelled pH as a function of added base is also show. The main recovered Fe, Al, Zn, Mn, and Mg precipitates are shown on the top of the figure. The graph shows the evolution of pH and the formation of solids as a function of base addition. If the formed phases were plotted as relative equilibrium composition against pH, then the resulting graph would resemble a typical (*T*, *x*)-diagram from Scheil–Gulliver analysis of primary precipitation used in metallurgy. The advantage of a

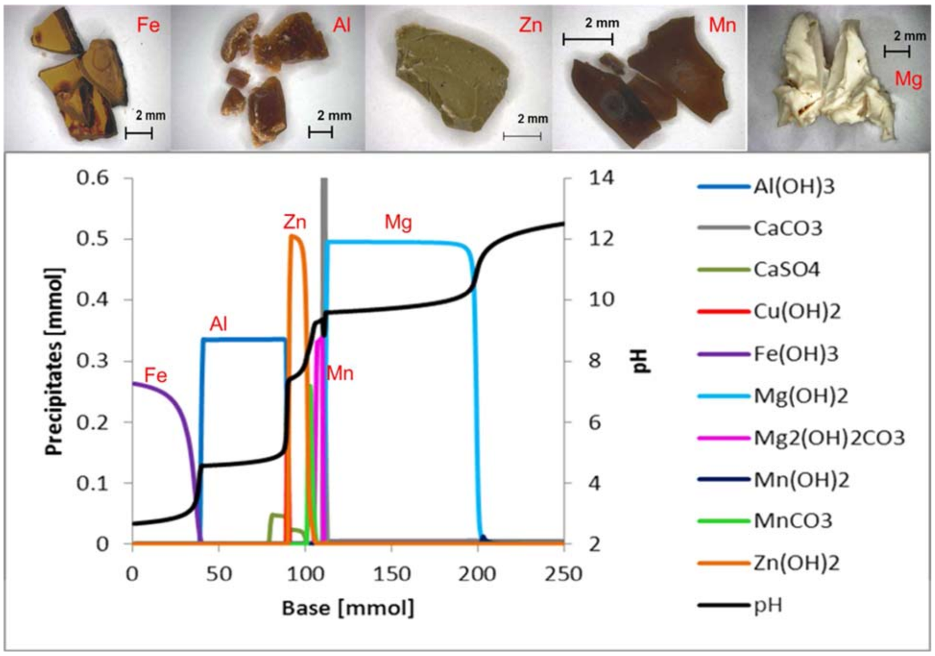

Figure 3. Order, identity, and magnitude of precipitates formed during titration according to the simulation.

The amount of carbon dioxide in the model has been adjusted to fit the experimental findings. The precipitates are in the order of appearance from the left: $Fe(OH)_3$, $Al(OH)_3$, $CaSO_4$, $Cu(OH)_2$, $Zn(OH)_2$, $MnCO_3$, $Mn(OH)_2$, $Mg_2(OH)_2CO_3$, $CaCO_3$, and $Mg(OH)_2$. The Purity P, Yield Y, and Selectivity S for recovered precipitates shown for main phases recovered (Fe, Al, Zn, Mn, and Mg) above were determined for Fe (P 95%, Y 97%, S 97%); Al (P 83%, Y 94%, S 94%); Zn (P 63%, Y 96%, S 96%); Mn (P 75%, Y 62%, S 61%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(pH, base) diagram is its immediate capability of permitting the experimental validation of theoretical predictions by measuring vs. base addition.

According to this thermodynamic model, the first precipitate filtered at pH 4 should contain iron hydroxide. The second precipitate filtered at pH 6 should be aluminum hydroxide and small amounts of calcium sulphate. This fraction may contain some copper hydroxide depending on the uniformity of pH near the endpoint and during filtration. The third fraction filtered at pH 9 should contain mainly zinc hydroxide and traces of calcium sulphate and manganese carbonate. The fourth precipitate collected at pH 10 should contain magnesium hydroxide with minor amounts of calcium carbonate and magnesium carbonate. The filtrations were done at pH values where the change in pH was most sensitive to the amount of base. Solid filtrates were collected at pH 3.6, 5, 8, 10, and 11. The solids removed contain the primary metals of interest, that is, zinc and copper. All but one precipitate were amorphous. The precipitate recovered at pH 11 had crystals identifiable by XRD. These crystals were $Mg(OH)_2$, $CaCO_3$, and Na_2SO_4.

Table 2 shows the distribution of each element in each precipitate relative to the total amounts recovered. Table 3 lists the amounts recovered relative to the amounts in the initial liquid (Table 1).

The iron precipitate obtained in this study could be used as water purification application and adsorption agent as well as for precipitating jarosite, $NaFe_3(OH)_6(SO_4)_2$, for example. The aluminum precipitate could be used as reagent in ettringite, $Ca_6Al_2(SO_4)_3$ precipitation for sulphate removal from mine waters. Sulphate is a general problem in natural fresh water systems if not controlled. Both hydroxide precipitates can be used for neutralizing acidic waste streams. More valuable base metal Cu, Zn, Mg, and Mg salts are valuable and can be forwarded into metals processing plants or chemical companies.

Ferric hydroxide in various states of hydration is rust brown and dominates the color of the first collected precipitate. The second precipitate contains mostly white aluminum hydroxide with iron and magnesium impurities. Aluminum hydroxysulfates may also be included in this precipitate.[22,23,27] The molar

Table 2. Experimental Results for the Separability of the Recovered Precipitates

Element	% (pH 2.6–3.6)	% (pH 3.5–5)	% (pH 4.9–8)	% (pH 7.7–10)	% (pH 10–11)
Cu	3	20	**76**[a]	0	0
Zn	1	2	**96**[a]	1	0
Fe	**97**[a]	3	0	0	0
Mn	2	4	33	**61**[a]	0
Ca	4	9	7	2	**79**[a]
Al	2	**94**[a]	4	0	0
Mg	0	2	2	7	**89**[a]
Na	7	**50**[a]	0	9	34
Co	0	0	**85**[a]	15	0
K	**72**[a]	0	21	6	0

The values are in mole fraction percentage of the total amount recovered for each metal. The values marked with "*" represent the primary precipitates for each pH interval.

[a] The primary precipitates for each pH interval.

Table 3. Experimental Yields in Percentage, that is, Amounts Recovered in Precipitates Compared to Initial Amounts in the Aqueous Phase

Element	% (pH 2.6–3.6)	% (pH 3.5–5)	% (pH 4.9–8)	% (pH 7.7–10)	% (pH 10–11)
Cu	4	2[a]	**94**[a]	0	0
Zn	1	2	**96**[a]	1	0
Fe	**97**[a]	3	0	0	0
Mn	2	4	33	**62**[a]	0
Ca	1	2	1	0	16
Al	2	**94**[a]	4	0	0
Mg	0	1	2	5	**68**[a]
Na	2	14	0	3	10
Co	0	0	**72**[ab]	18	0
K	8	0	2	1	0

The numbers are mole fractions. The values marked with "*" represent the primary precipitates for each pH interval.

[a] The primary precipitates for each pH interval.

[b] estimated

ratio of aluminum to sulfur was 9:4. The precipitate contained less than 4% silicate, which has a small effect for the precise pH where precipitation begins.[22] The third precipitate is white zinc hydroxide with traces of green copper hydroxide. The amount of trace metals especially rare earth and transition metals is high in this fraction. The magnesium carbonates and hydroxides in the fourth precipitate are white. The strong brown color in the fourth precipitate is probably due to a mixture of oxidized manganese compounds. The fifth and last precipitate is dominated by white magnesium and calcium hydroxides. Crystals of magnesium hydroxide $Mg(OH)_2$, calcium carbonate $CaCO_3$, and sodium sulphate Na_2SO_4 were identified by XRD. Quantitative agreement between computational and experimental efforts was achieved by fine tuning the unbound model parameters, that is, CO_2 adsorption and pH sampling points. The model suggests that the precipitates are $Fe(OH)_3$, $Al(OH)_3$, $CaSO_4$, $Zn(OH)_2$, $MnCO_3$, $Mg_2(OH)_2CO_3$, $CaCO_3$, $Mn(OH)_2$, and $Mg(OH)_2$.

The metal cations precipitate at slightly different pH values than the model predicted. This is a common feature when titration curves are compared with respective equilibrium models and has been previously pointed out in AMD studies.[21] If the time between the additions of alkaline is shorter than the time necessary to reach chemical equilibrium, all features on the curve are smoothened. Even though the acid–base reactions are generally quite fast, gas adsorption, precipitation, presence of solids (nuclei), or any other ion exchange processes will delay the attainment of chemical equilibrium. Another feature is the character of the titration curves in the range where the solution turns to be strongly basic. In the earlier work of Totsche and coworkers,[21–23] it was suggested that the gentle slope around pH 8 results from the ion exchange of surface complexes. They showed experimentally that removing the aluminum and iron precipitates eliminates the slope.[23] They have also proven that a long enough equilibration time leads to the same result, that is, it eliminates the slope.[21] The assumption of surface complexes is, however, somewhat problematic, as it incorporates a less well defined (temporary) thermodynamic component into the calculation system. They conclude that the calculated metal values provide estimates, which are yet to be confirmed by precise elemental analysis.[21] However, according to the Gibbs'ian model based solely on thermodynamically well-defined species, the precipitated iron oxides/hydroxides will meld with other solids formed at pH 5–9. If the precipitates were not removed, this could be observed as a relative retardation of attaining pH stability in this pH range. Aluminum oxides and silicates would do the same with most of the precipitates formed in this pH region (pH 5–9). Filtering away the precipitates at specific pH-thresholds then obviously serves to simplify the thermodynamic system for a better computational reproduction of the experimental results. By confirming the experimental setup to the computational modelling of the physical and chemical processes in aqueous multiphase solution, the simulations works well for AMD titrations covering the range of experimental conditions encountered. As the methods are quite generic, it is anticipated that they can be used not only for the determination of neutralization capacities, but also for improved metals control and for predicting the outcome of mixing process streams. The Gibbs'ian model appears to be a useful and quantitative tool for designing processes for the discerning recovery of mine water metal content. Collaboration between modelling and experimental work could be used to improve the selective recovery of valuable metals from the mine water.

Biohydrometallurgical Recovery of Gold from Waters

Hydrometallurgy is defined as a field of metal processing that is connected to water and hydrometallurgical separation methods are those in which one or more of the phases involved in the process is aqueous. It has been said that modern hydrometallurgy began with the cyanide process for gold recovery.[42] Hydrometallurgical solutions are typically generated by dissolving metals present in the raw materials in acids or bases. Metals can be, and are often separated in the dissolution step when one or more of the metals is not soluble in the solvent used. Hydrometallurgical separation is often performed by chemical or biochemical precipitation, solvent extraction (liquid-liquid extraction) or by means of solid ion exchangers.[43] These methods were first used for the separation of rare earth elements (REE) and actinides, but soon their application spread to all kinds of metals, including gold, other precious metals, and base metals.[44]

Bioleaching was developed over 60 years ago and biohydrometallurgy is today a widely studied area of hydrometallurgy.[45] It is often used in the treatment of mine effluent[46–48] and for recovery of metal from secondary raw materials.[49,50]

Biosorption is one interesting and naturally existing phenomenon and has been applied for gold recovery. Two recovery methods for gold are briefly described in this work: *biosorption* using in-house grown fungal matter into filter cartridge and *solvent extraction of gold using task-specific ionic liquid.*

Biosorption of Gold

While the most common bioprocessing methods, bioleaching and biologic sulphate reduction are based completely on bacterial activity, also metabolism-independent passive biochemical phenomenon can be inspiring for biohydrometallurgy. For example, a technique called biosorption uses the ability of certain biomasses to bind and concentrate dissolved elements from liquid streams. Adsorption of heavy metals is usually due to functional groups, like carboxylate, hydroxyl, amine, phosphoryl and others, located within cell wall

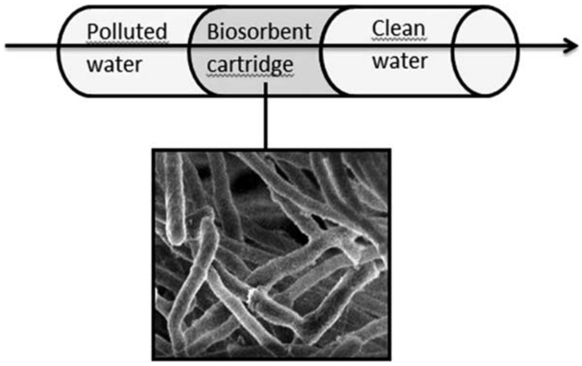

Figure 4. Water treatment with self-immobilizing fungal biomass cartridge.[61]

structures.[51–53] Valuable metals, like gold, silver, platinum group and REE can be captured selectively due to thiol groups, chitosan, sericin, resins, and especially with their modifications.[54,55] Different biosorbents studied are bacteria, fungus, algae, plant biomass, wastes, and others; biomass may be collected from the environment or cultivated separately.[51–56]

The strength of biosorption is fast adsorption kinetics and high capacity.[51,58] However, despite promising results, this technique is not yet used in industrial scale applications. This is mainly due to drawbacks related to traditional approach utilising freely suspended biomass. In these systems, biomass-liquid separation is challenging and clogging may occur.[59,60] Therefore, research has moved on to immobilization of biomass with different carrier matrices, which can be chemical products or biomass-based.[57,59,60]

Our approach for solving the challenges is a self-immobilizing fungal biosorbent. Figure 4 shows the basic biosorption process and SEM image of fungal matter. Rapid growth of certain fungus and their dense mycelia structure allow producing biosorbent units with different three-dimensional (3-D) shapes. It has been noticed that the adsorption capacity is not remarkably decreased when moving from freely suspended fungal biomass to self-immobilization. Therefore, self-immobilizing fungal biosorbents offer opportunities for industry due to their high-sorption capacity, fast binding kinetics, high liquid permeability and easy use. The applications may range from nonselective heavy metal removal from waste waters (e.g., AMD)[51,53,60,61] to selective accumulation of gold and REE into the biomass.[54–56,59] Separate study also showed the fungal matter used for gold in this work was able to purify mine water from metals but it showed less selectivity with other metals.

One example of experimental work is the search for highly gold-selective fungal species. Three different fungal strains, namely *Phanerochaete chrysosporium*, *Trichoderma reesei*, and *Cladosporium cladosporioides* were cultivated and self-immobilized to a form of thin film, with a fabric carrier material to further strengthen the structure. The aim is to develop an easy-to-use cartridge system for separation and development is ongoing with novel carrier material development and finding more selectivity within aqueous species.

Average biomass weight of films was 0.14, 0.05, and 0.23 g, respectively. Films were placed to filtering columns and 40 mL of Au(III)-chloride solution (98 mg L^{-1} total dissolved Au, pH 2.3) was gravitationally passed through the biomass. Filtrated solution was measured with ICP-MS for gold. Au(III) removal rates percentage and binding capacities were measured in a single biosorption for three different fungal species:

- *P. chrysosporium*: 91% and 27 mg g^{-1} biomass
- *T. reesei*: 52% and 46 mg g^{-1} biomass
- *C. cladosporioides*: 56% and 10 mg g^{-1} biomass.

P. chrysosporium was the most rapidly growing fungus but with moderate Au(III) capacity. However, *T. reesei* was found to possess very high capacity for Au(III), but unfortunately, it grows more slowly. *C. cladosporioides* showed the least potential for gold removal. It should be mentioned that the fungal matter does not have to be alive for retaining the biosorption activity. Also the fungal matter can be in rest in a dry media for years and wake up in the presence of water again. Further work will be carried out to understand the biophysicochemical mechanisms behind selectivities, binding, development of the recovery application, improving the growth rate of the fungal matter, and testing new aqueous medias.

Solvent Extraction of Gold Using Task-Specific Ionic Liquid

Another topic separation method was tested in this work for separation of gold from aqueous solutions. Solvent extraction has been applied to separate almost every metal element, and it is also widely applied in the separation of organic compounds.[62–64] In solvent extraction, metals are extracted with a suitable reagent to a water-insoluble organic phase, which is typically, for example, a kerosene-based hydrocarbon solvent. While mixing, one of the phases is dispersed within the other one creating large surface area, over which the extractable species moves to the other phase.[66,67] Solvent extraction reagents have traditionally been divided into three groups.

1. Acidic extractants that extract metals either by chelating or a cation exchange mechanism, and includes organophosphoric acid derivatives or carboxylic acids or hydroxyoximes.
2. Amine extractants, which are either strong (quaternary amines) or weak (secondary and tertiary amines) anion exchangers.
3. Ethers, esters, ketones, aldehydes, and alcohols, together with organophosphoric acid derivatives with oxygen or sulfur as an electron donor atom.

The metal interacting molecule extractant, for example, di-2-ethyl-hexyl phosphoric acid (DEHPA) is dissolved into solvent *e.g.* kerosene. The mechanism involves the solvation of neutral inorganic molecules or complexes.[43,65]

Ionic liquids are solvents that are composed of only cations and anions. These solvents have been also studied for their use in extraction of metals from water. The development of new task-specific ionic liquids have shown promising advancement but they have not yet reached large scale plant size operation.[65–79] Pure ionic liquids have been found to extract metals directly from aqueous phase including gold. In this work octylmethyl imidazoliumbistrifluorosufonylimide [OMIM][TFSI] was used to extract gold from pure gold chloride solution and from gold leachate solution including impurities. Three different extraction agent combinations were used with these two starting solutions 1) [OMIM][TFSI] 2) DEHPA-[OMIM][TFSI] 3) DEHPA-Kerosine. In both cases water to organic ratio was 5:1 and the mixing time was 1 hour in a shaker at 25°C. After shaking, the solutions were centrifuged and samples were taken from the aqueous phase to determine the degree of gold extraction. First the extraction was carried out for synthetic gold chloride solution. High extraction yields were found for gold in

Table 4. Distribution Coefficients for Solvent Extraction of Gold from Real Leachate Solution Using Three Extractions Agent Combinations: (DK) DEHPA-Kerosene, (D+IL) DEHPA-Ionic Liquid, and (IL) Pure Ionic Liquid

	Au	Mg	Al	Cu	Fe	Mn	Zn	Ni
DK	52	0	17	0	>130	0	1	0
DIL	>58	0	3	0	>130	0	1	0
IL	>58	0	0	0	0	0	0	0

The analysis of the metals composition is from the aqueous phase.

cases 1) and 2) for one stage process. Extraction results for gold from synthetic $AuCl_4^-$ solutions were as follows:

1. IL-solution (IL): >99% gold extracted
2. DEHPA-IL-solution (DIL): >99% gold extracted

Extraction of gold was further tested in multicomponent gold leachate solution containing Au, Mg, Al, Cu, Fe, Mn, Zn, Ni metals. Extraction yields for gold were found to be high:

1. IL-solution (IL): >92% gold extracted
2. DEHPA+IL-solution (DIL): >92% gold extracted
3. DEHPA+kerosene-solution (DK): 91% gold extracted

Table 4 shows the extraction results for real leachate of gold. Distribution coefficient and yields are shown with [OMIM][TFSI] and with combinations with DEHPA and kerosene. The distribution coefficient D was defined from the aqueous phase analysis prior $C_{i,aq}$ and after $C_{f,aq}$ the extraction and the volume ratios of the aqueous phase V_{aq} and ionic liquid phase V_{IL}. The distribution coefficient is defined in the Eq. 1.

$$D=\frac{C_{f,IL}}{C_{f,aq}}=\frac{C_{i,aq}-C_{f,aq}}{C_{f,aq}}\frac{V_{aq}}{V_{IL}} \tag{1}$$

The results show high separation of gold from multicomponent solution in all solvent combinations. Using pure ionic liquid [OMIM][TFSI] one can separate gold from different leachates.

Discussion

Stricter effluent discharge limits have been proposed for metal mines in many countries. In the northern hemisphere, the challenge has been the excess of water after heavy rains and melting of snow but as commonly in many arid areas the challenge is related to water scarcity. In both these cases, tendency and need in the mines is to reuse and recycle more water in order to gain public and regulatory acceptance.

The highly acidic extremely metal rich AMD investigated here needs to be neutralized before discharge. A cost effective water treatment method that selectively precipitates metalliferous compounds would allow the utilization of the metals in these large wastewater streams and may thus become an additional source of revenue. Through collaboration between modelling and experimental work, a base titration procedure was developed to selectively separate metals in a sample AMD from the Pyhäsalmi Mine. Apart from copper and zinc, the selective separation titration would also allow the recovery of, for example, iron and aluminum. Compared to neutralizing the acid, the recovery of copper and zinc comes at a relatively small additional expense. Filtering away the precipitates at specific pH-thresholds serves a dual purpose. It improves selectivity of metal recovery and reduces the modelling effort required to computationally reproduce the experiments. The experimental results were in good agreement with the thermodynamic model. This study is an example of benefits arising when modelling is performed concurrently with experimental efforts.

Bio- and hydrometallurgical separation methods are being used in extractive metallurgy increasingly and it is likely to have a significant role in sustainable metallurgical industry.

Solvent extraction and biosorption methods are developing for metals recovery. Alternative extractants are studied intensively in metals' separation and purification. With these methods, the target metal(s) may also be concentrated during the separation step. Solvent extraction is being used in processing secondary raw materials, because among previously mentioned features, it is known to be flexible and can readily be modified to cater for complex and varying raw materials. The extraction yields for gold using ionic liquids show good potential for their use in metallurgical systems. Searching for gold selective, self-immobilizing fungal biosorbents and testing their performance with stock and complex solutions were carried out. Au-selective biosorption was good with *P. chrysosporium* fungal species. *P. chrysosporium* binding capacity was 27 mg Au/1 g biomass or better. Binding capacity was not changed when plenty of other elements were present in solution. Typical selectivity for other metals than gold was found to be 20% and depends on the solution.

The future work will focus on finding and designing more functionalities and applications with hydrometallurgical separation methods, thermochemical modelling and analytics. Also further studies are carried out with ionic liquids applications in extractive metallurgy and for fungal matter as biosorption material. Special interests are application for precious metals removal and separation of REE and related thermodynamic models.[80–82] The durability and selectivity of both ionic liquids and fungal matter with different solutions should be demonstrated. New combinations, methods and hybrid processes result improved resource efficiency and provide solutions and technologies for selective recovery and better environment.

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