

Environmental Science Processes & Impacts

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



rsc.li/process-impacts

Cite this: DOI: 10.1039/c0xx00000x

Full paper

www.rsc.org/xxxxxx

Lead sulfate nano- and microparticles in the acid plant blow-down generated at the sulfuric acid plant of the El Teniente mine, Chile**Giancarlo M. Barassi,^a Martin Klimsa,^a Thomas Borrmann,^{*a} Mathew J. Cairns,^a Joachim Kinkel^b and Fernando Valenzuela^c**⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

The acid plant ‘blow-down’ (also called weak acid) produced at El Teniente mine in Chile was characterized. This liquid waste (tailing) is generated during the cooling and cleaning of the smelter gas prior to the production of sulfuric acid. The weak acid was composed of a liquid and a solid phase (suspended solids). The liquid phase of the sample analyzed in this study mainly contained Cu (562 mg.L⁻¹), SO₄²⁻ (32800 mg.L⁻¹), Ca (1449 mg.L⁻¹), Fe (185 mg.L⁻¹), As (6 mg.L⁻¹), K (467 mg.L⁻¹) and Al (113 mg.L⁻¹). Additionally, the sample had a pH-value and total acidity of 0.45 and 2970 mg.L⁻¹ as CaCO₃, respectively. Hence, this waste was classified as extremely acidic and with a high metal content following the Ficklin diagram classification. Elemental analysis using atomic absorption, inductively coupled plasma, X-ray diffraction and electron microscopy showed that the suspended solids were anglesite (PbSO₄) nano- and microparticles ranging from 50 nm to 500 nm in diameter.

Introduction

El Teniente is a copper mine operated by the state owned company Corporación Nacional del Cobre (CODELCO) located in the Andes mountains range near Rancagua in Chile. The mine extracts copper and molybdenum sulfides, which are separated by ore selective flotation. El Teniente is considered to be the world’s largest underground copper mine in size and 5th in terms of production of copper.¹ It operates two ‘Teniente-type’ furnaces, which are 22 metres long and 5 metres wide, located at Caletones (34° 07’ S and 70° 27’ W) near the mining site, granting the mine a production capacity of 400,000 tonnes of copper per year.¹

Roasting of sulfide containing minerals generates gases with a high content of SO₂ and suspended particulate material. The chemical composition and physical characteristics of this gaseous effluent are in direct relation to the mineral being roasted and the furnace employed. In the past, no post-treatment of the gases released from the furnaces was carried out, which led to the release of gases containing SO_x and particulate material containing As and various metal compounds to the surrounding environments. The contribution to pollution derived from copper roasting in this particular region of Chile was investigated by Romo Kröger et al.,² who reached the conclusion that aerosols containing Cu, Zn, As and S were produced by the smelter contributing significantly to the atmospheric contamination in the area. Another study showed that these aerosols were transported away from the site by wind currents and contributed to abnormal concentrations of heavy metal and metalloids in surrounding rivers and waterways.³

In order to meet current environmental standards in Chile for the discharge of gases, treatment of the exhaust from the smelter was installed.^{4,5} Now the exhaust is thoroughly scrubbed and sulfur is transformed into a valuable commodity (sulfuric acid) before the remainder of the gases is released into the environment. Most sulfide smelters have a sulfuric acid plant attached to make use of the generated SO₂ to produce sulfuric acid as a by-product. During the gas-cleaning step, the exhaust gas is channelled through water scrubbing towers operating in counter current. As the gases cool down particulate material, some of the SO₂ and other gases are trapped in the condensate of the water vapour. This condensate is commonly known as acid plant ‘blow-down’ or also referred to as weak acid in the literature.^{1,6,7} The next step of the exhaust purification involves an electrostatic precipitator, which further removes fine particles suspended in the gas stream. This is important, as the SO₂ current must be free of any particulates before contacting it with a V₂O₅ catalyst, which oxidizes SO₂ to SO₃, as particles could damage the catalyst or impede gas flow. Finally, the freshly generated SO₃ is contacted with water to form concentrated sulfuric acid.

The copper sulfides targeted for copper mining at El Teniente are a constituent of an ore containing arsenic, molybdenum and lead impurities amongst others. Hence, the weak acid from El Teniente is expected to contain high concentrations of arsenite and sulfate as well as traces of various other elements.^{6,7} The weak acid stream is regularly analyzed for arsenic and sulfur compounds and for its acidity. The weak acid is treated in order to meet environmental discharge requirements described by regulations, Decreto Supremo 90 in Chile.⁸ The chemical

treatment of the weak acid consists of two stages. The first one involves the addition of milk of lime $\text{Ca}(\text{OH})_2$ to precipitate heavy metal ions as hydroxides $\text{Mn}^+(\text{OH})_n$, sulfate as gypsum CaSO_4 and arsenic as calcium arsenite CaAsO_3 .^{6,7} The second stage involves the addition of ferric chloride and hydrochloric acid to precipitate any remaining arsenic from solution. The resulting precipitates form a sludge, which will be referred to in this work as 'dirty gypsum' and contains a mixture of calcium sulfate, calcium arsenite and ferric arsenite.⁷ These inorganic salts have low solubility products. Therefore, the 'dirty gypsum' is considered 'safe' for disposal on landfills with only minor leaching issues occurring. However, it should be noted that arsenites are soluble in strongly acidic environments.

Although weak acid is periodically surveyed at El Teniente to determine the content of sulfate, As and suspended solids, little attention has been given to the nature of the suspended solids (microparticles, nanoparticles) or to the presence of metal ions in the liquid. As some of the particulate material is very fine (nanoparticles) and contains heavy metal species it could pose a threat towards the environment and human health. Even after being occluded by the dirty gypsum during the addition of milk of lime to the weak acid, small particles could be transported away by mechanisms similar to those proposed by Romo-Kröger et al. in their study.³ Romo-Kröger et al. found that especially wind erosion and the transport of aerosols, small particles (dust) and gases were responsible for the spread of contaminants.

In the literature most studies of the gaseous effluent have placed emphasis on the recovery of valuable metal ions from the flue dusts collected downstream at the electrostatic precipitator and have neglected the weak acid waste.⁹⁻¹¹ This work focuses on the analysis of the acid plant 'blow-down', also known as weak acid, generated by water scrubbing towers. The analysis is meant to be a first step to assess the environmental risk and commercial opportunities posed by this waste stream.

2. Experimental Procedures

Sample Characterization

Two samples (1.0 L each) of Caletones smelter weak acid were collected by us at the El Teniente mine on the 10th of August 2010 and were stored in a padded container and taken to Hidrolab Ltda in Santiago, Chile, a private laboratory holding ISO 17025 certification, to be analysed in terms of their ionic constituents, solids, pH, chemical oxygen demand, acidity and conductivity. The samples were chosen to represent a good cross-section of the weak acid usually discharged. The probability of species being present in the sample based on an analysis of the original ore, environmental concerns and potential recovery applications was taken under consideration. Three key parameters of the samples collected by us were compared to process data provided by CODELCO. The content of dissolved As, SO_4^{2-} and % w/w of suspended solids, were provided directly from the process engineer in charge of the operation of the sulfuric acid production plant at El Teniente. In this work, data collected from May 2010 until October 2010 is presented. Control charts were plotted for the data in order to monitor and understand the long-term operation of the sulfuric acid plant, the quality of the weak acid being discharged and to place the samples collected into context.

Characterization of Suspended Solids

A 50 mL aliquot of the liquid weak acid sample containing suspended solids was allowed to settle under ambient conditions over night. The supernatant liquid was removed. A small amount of liquid was left behind covering the surface of the solids. These wetted solids at the bottom of the sample container were scrapped out with a spatula and placed on a watch glass and dried at 383 K for 24 h.

The solids were homogenized and used for different analysis techniques. A portion of the dried sample was dusted onto carbon tape fixed to an aluminium SEM sample holder. The sample was coated with platinum and analyzed using a JEOL 6500-F scanning electron microscope (SEM), equipped with energy dispersive spectroscopy (EDS) and backscattered electron detector.

Another portion of the solids was studied using a X'PERT PRO PANALYTICAL X-Ray Diffractometer equipped with anode material Cu, $\lambda = 1.54060 \text{ \AA}$, as a radiation source. The X-Ray Diffraction (XRD) pattern was obtained and compared against reference patterns from the powder diffraction file, version 4+, from International Centre for Diffraction Data, ICDD, Pennsylvania USA.

A small portion of 182.2 mg of the suspended solids was digested in aqua regia and analyzed using Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Flame Atomic Absorption Spectroscopy (FAAS) in Nuremberg, Germany at the Georg-Simon-Ohm Hochschule. The instruments used were a Thermofisher ICAP-6200 and GBC 906 respectively.

Results and Discussion

Operation of cooling towers

Weak acid samples were collected from the two cooling towers at El Teniente's sulfuric acid plant. Both towers produce an overall of 500 m³ day⁻¹ of weak acid with an average temperature at the outlet of 328 K. Similar flows have been reported for other plants, for example, Toyo's smelter in Japan generates 300 m³ of weak acid per day.¹²

The liquid had a light blue colour containing particulate material in suspension, which settled within minutes after sample collection. An analysis of the suspended solids as well as the concentrations of arsenic and sulfate in the supernatant is presented below. Although a light blue colour could be observed for the liquid portion of the sample (characteristic of copper sulfate in solution), little attention has been paid to the metal content of this effluent in the past. A potential reason might be that the dissolved copper concentration of the effluent was estimated to be quite low, which makes this waste unattractive for hydrometallurgical processes and copper recovery.

CODELCO staff members provided operational data for the two water scrubber towers at the acid generation plant of the El Teniente mine, collecting data three times a day over a period of 6 months from May 2010 until October 2010. **Figures 1a) to 2c)** show Stewart charts, also known as control charts for plant 1 (**Figures 1a) to 1c)** and for plant 2 (**Figures 2a) to 2c)**), recording the total concentrations of sulfate (**1a)** and **2a)**) and arsenic (**1b)** and **2b)**) as well as the weight percentages of suspended solids (**1c)** and **2c)**). The charts present the average

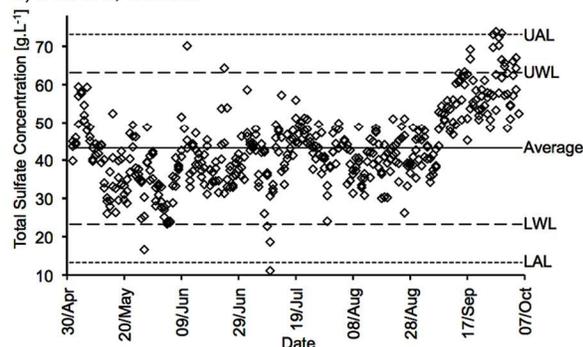
values for the variables analyzed over time (solid lines), the lower and upper warning limits (LWL and UWL), $\pm 2\sigma$ from the average (dashed lines), and the lower and upper action limits (LAL and UAL), $\pm 3\sigma$ from the average (dotted lines). If the limits had negative values they were not depicted. Approximately 99.7% of the results fell inside the limits. If any measurement data outside the LAL or UAL was found immediate action was taken to bring the operational output back close to the average. The variations in the measurements were due to the nature of the ore processed.

	As [$\text{mg}\cdot\text{L}^{-1}$]	SO_4^{2-} [$\text{g}\cdot\text{L}^{-1}$]	Suspended solids [% w/w]
Average	6.1	43.2	0.23
Std. dev.	2.9	10.0	0.63
min	1.8	11.1	0.03
max	65.0	73.8	13.00
UWL	11.9	63.1	1.49
LWL	0.3	23.2	neg. value
UAL	14.7	73.1	2.12
LAL	neg. value	13.2	neg. value

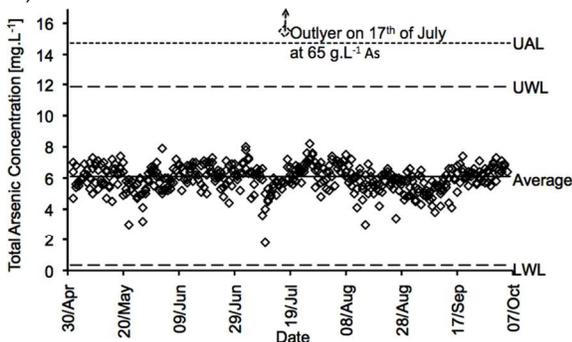
Plant 2

	As [$\text{mg}\cdot\text{L}^{-1}$]	SO_4^{2-} [$\text{g}\cdot\text{L}^{-1}$]	Suspended solids [% w/w]
Average	6.5	68.7	0.97
Std. dev.	1.2	11.6	0.95
min	3.1	39.8	0.06
max	11.5	108.5	9.82
UWL	9.0	91.9	2.88
LWL	4.0	45.5	neg. value
UAL	10.3	103.5	3.83
LAL	2.8	33.9	neg. value

a) Plant 1, Sulfate



b) Plant 1, Arsenic



c) Plant 1, Solids

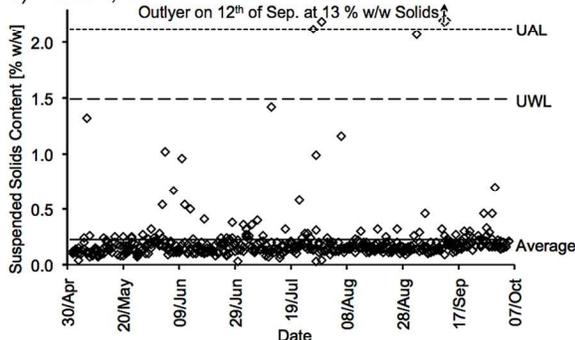


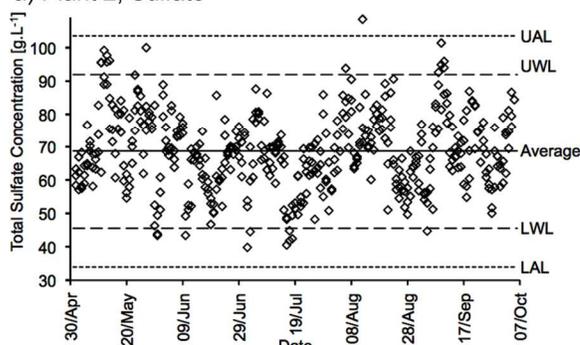
Figure 1: Control charts for plant 1 showing sulfate (1a), arsenic (1 b) and solids (1 c) contents in the weak acid over the period of time studied.

Table 1 presents the statistical parameters of the operation and summarizes the values presented in **Figures 1** and **2**. Values of LWL and LAL for some of the parameters are not shown since they gave negative values and there cannot be negative concentrations.

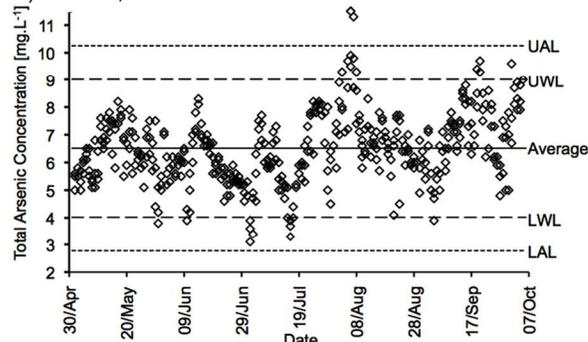
Table 1: Summary of the presented control chart parameters for the weak acid generated at plants 1 and 2 at El Teniente.

Plant 1

a) Plant 2, Sulfate



b) Plant 2, Arsenic



c) Plant 2, Solids

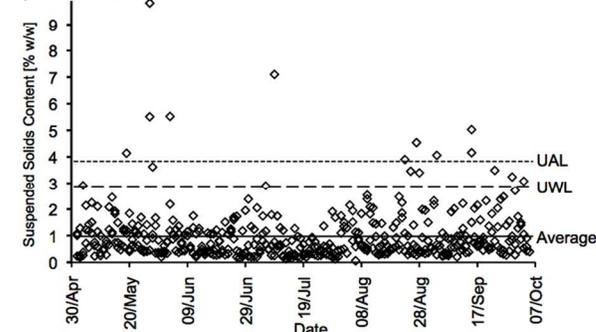


Figure 2: Control charts for plant 2 showing sulfate (2a), arsenic (2b) and solids (2c) contents in the weak acid over the period of time studied.

Figures 1 and **2** showed that the two samples studied throughout this article were collected, when the plant was

operating within 1σ of the average, indicating that the samples were a good representation of a normal operational day.

As and SO_4^{2-} concentration data for plant 1 were less dispersed than data for plant 2. On the 16th of July 2010, plant 1 reported the maximum value for As during the monitored time with a concentration 65 mg.L^{-1} for this species in solution. This value contributed to the large standard deviation of 2.9 mg.L^{-1} for the arsenic concentration measured at this plant of El Teniente. The average amount of suspended solids in plant 2 was four times larger than in plant 1. The concentration of SO_4^{2-} reached a peak value of 108.5 g.L^{-1} on the 11th of August at plant 2. Despite these differences, overall, both plants operated steadily. Less than 10 events where the parameters exceeded LAL or UAL values (located at $\pm 3\sigma$ from the average) occurred during the monitored period.

A study done by Inami et al on the weak acid generated at the Toyo smelter, Japan,¹³ reported the following values for the major constituents: $80 - 150 \text{ g.L}^{-1} \text{ H}_2\text{SO}_4$ and $2 - 5 \text{ mg.L}^{-1} \text{ As}$. While the values for the average arsenic concentrations at El Teniente were higher than those reported for the Toyo smelter, they were still within the standard deviation (1σ). The values for sulfate at El Teniente were about half those observed at Toyo but also within the standard deviation (1σ). This indicates that the data collected for this study can provide insights into processes at other, comparable plants as well. Further studies of weak acid from Huelva, Spain and Toyo, Japan confirm this although the arsenic content at the Spanish plant was even lower than at the Toyo smelter.⁶ The differences could be attributed to the quality of the ore being processed at the smelters.

30 Chemical characterization of the liquid phase, the supernatant

Two representative samples of weak acid waste were collected by CODELCO at the sulfuric acid plants at El Teniente. The samples were combined to average out any inconsistencies and filtered. The liquid phase was analyzed in a private laboratory in Chile. The results from the chemical analysis of the liquid phase of the sample are displayed in **Table 2**.

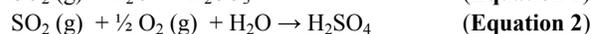
Table 2: Chemical analysis of the liquid portion of the samples.

Analyte	Value	Unit	Analyte	Value	Unit
Al ³⁺	113	mg.L ⁻¹	Ni ²⁺	0.402	mg.L ⁻¹
As, total	6.0	mg.L ⁻¹	Pb, total	22	mg.L ⁻¹
As ^a	6 ± 3	mg.L ⁻¹	V, total	<0.008	mg.L ⁻¹
As Toyo ¹³	2-5	mg.L ⁻¹	Cl ⁻	475	mg.L ⁻¹
As Huelva ⁶	1	mg.L ⁻¹	NO ₃ ⁻	<0.20	mg.L ⁻¹
Ca ²⁺	1449	mg.L ⁻¹	SO ₄ ²⁻	32.8	g.L ⁻¹
Co, total	0.103	mg.L ⁻¹	SO ₄ ²⁻ ^a	56 ± 20	g.L ⁻¹
Cr, total	0.076	mg.L ⁻¹	SO ₄ ²⁻ Toyo ¹³	80-150	g.L ⁻¹
Cu ²⁺	562	mg.L ⁻¹	SO ₄ ²⁻ Huelva ⁶	120	g.L ⁻¹
Cu ²⁺ Toyo ¹³	0.5-1	g.L ⁻¹	COD	3023	mg.L ⁻¹
Cu ²⁺ ¹⁴	1.1	g.L ⁻¹	Conductivity	334000	μS.cm ⁻¹
Fe, total	185	mg.L ⁻¹	pH	0.45	
K ⁺	467	mg.L ⁻¹	Acidity	2970	mg CaCO ₃ .L ⁻¹
Mg ²⁺	39.7	mg.L ⁻¹	Solids	0.95	% w/w
Mo, total	50.3	mg.L ⁻¹	Solids ^a	1 ± 1	% w/w
Na ⁺	152	mg.L ⁻¹			

^a Average operational parameters taken from the control charts for El Teniente, **Figure 1** and **2**, **Table 1**, (values for Plant 1 and Plant have been combined for this comparison).

The major components, with concentrations $>100 \text{ mg.L}^{-1}$, in

the weak acid were H⁺, Cu²⁺, SO_4^{2-} , Ca²⁺, total Fe (Fe²⁺ and Fe³⁺), total As, K⁺, and Al³⁺ (**Table 2**). Consequently, this liquid waste can be categorized as extremely acidic and high in metal content according to the Ficklin diagram.¹⁵ The low pH value of 0.45 may be explained from the formation of sulfurous acid and sulfuric acid due to the presence of SO₂ in solution. The reactions of SO₂ in presence of water under anoxic and oxidizing conditions are represented in **Equations 1** and **2** respectively.



Both of these acids are polyprotic in nature meaning that the degree of protonation of the acid in solution will depend on their respective pK_a values. Sulfurous acid has a pK_a value for the first deprotonation of 1.90 and for the second deprotonation of 7.29. Therefore the species most likely present in the sample was H₂SO₃. On the other hand, sulfuric acid has a pK_a value for the first and second deprotonation of -3.0 and 1.99 respectively. Consequently the predominant species was HSO₄⁻. For this study it was assumed that a mixture of H₂SO₃ and HSO₄⁻ was present in the sample.

The high value for the Chemical Oxygen Demand (COD) of 3023 mg.L^{-1} may be attributed to the presence of As⁵⁺ and H₂SO₃, which can be oxidized to As⁵⁺ and sulfuric acid respectively.

Taking under consideration the volume of weak acid produced per day and the concentration reported in **Table 2**, it was estimated that approximately 100 tonnes of copper are expelled through the fumes of this copper smelter of El Teniente into the weak acid waste each year. This estimated loss in copper was about half of the losses estimated by Ivšic-Bajceta for a smelter in Serbia.¹⁴ Considering the actual copper price this presents a significant loss of commodities and economical value. Using the composition of the weak acid of El Teniente as a basis, a model for the recovery of copper from this waste stream has been developed as part of a PhD thesis.¹⁶ This model describes the formation of 'dirty gypsum' and the potential recovery of copper using a silicate sorbent. The model was presented as an alternative to copper recovery solutions already implemented at other smelters. For example, at Toyo's smelter copper ions present in the weak acid are precipitated as copper sulfide by the addition of NaHS to counter exactly these losses in copper.¹² It would be interesting to compare the effectiveness and relative costs of the sulfide treatment and the use of silicate sorbents in future studies. For convenience an excerpt of the PhD thesis has been provided as supplemental information.

Molybdenum was only present at about an 11th of the level of copper; however, this means that about 9 tonnes of molybdenum are disposed with the weak acid each year. Similar losses of molybdenum were not reported for the Toyo or Serbian smelter owing probably to the composition of the local ore. It also appears that the relative levels of molybdenum to copper in the weak acid waste investigated in this study were quite high compared to other wastes for example flue dust.⁹ Further research would be required to investigate this and the nature of the molybdenum compounds in the future.

The amount of lead in the sample was less than half the amount of molybdenum and only about a 26th of the amount of copper. On first glance this appeared unremarkable but is discussed further below.

Characterization of the solid phase: suspended particles.

The suspended solids portion of the representative sample of the sulfuric acid plant at El Teniente was separated from the supernatant by settling and filtration as detailed above. The sample was dried for X-ray analysis and electron microscopy. A further portion of the suspended solids was dried and subsequently digested in aqua regia and analyzed for the content of heavy metals and metalloids using ICP-OES and FAAS). Results from the chemical analysis are shown in **Table 3**.

Table 3. Concentration of different metal and metalloids in the suspended solids of the weak acid

Analyte	Concentration [mg.g ⁻¹]	Analyte	Concentration [mg.g ⁻¹]
Al	0.22 ± 0.01	Mo	<LOD
As	1.65 ± 0.02	Na	0.11 ± 0.01
Ba	<LOD	Nb	0.007 ± 0.002
Bi	1.20 ± 0.01	Pb	635 ± 17
Ca	1.20 ± 0.01	Re	<LOD
Co	0.002 ± 0.002	Sb	0.24 ± 0.01
Cr	<LOD	Si	<LOD
Cu	10.0 ± 0.3	Sn	0.02 ± 0.01
Fe	6.5 ± 0.3	Ti	0.01 ± 0.01
Hg	0.11 ± 0.01	V	0.009 ± 0.005
K	0.64 ± 0.15	Y	<LOD
Mg	0.04 ± 0.01	Zn	0.45 ± 0.01
Mn	0.007 ± 0.002	Zr	0.008 ± 0.002

The sample was mainly composed of lead with a concentration of 635 ± 17 mg.g⁻¹. High Concentrations of lead might be explained from the presence of galena, a lead sulfide (PbS), which is commonly found in ores containing copper sulfides. The solids were not washed and consequently the sample contained impurities from the supernatant depending on their levels. As expected some copper, iron, potassium, calcium and arsenic were found in the sample. Furthermore bismuth was present, which was not included in the analysis of the supernatant sample. Other constituents were only present at low levels, a few below the limit of detection (LOD) of the analysis methods employed. These findings indicated that the suspended solids were mainly comprised of lead compounds. In the following it will be attempted to identify the specific compounds.

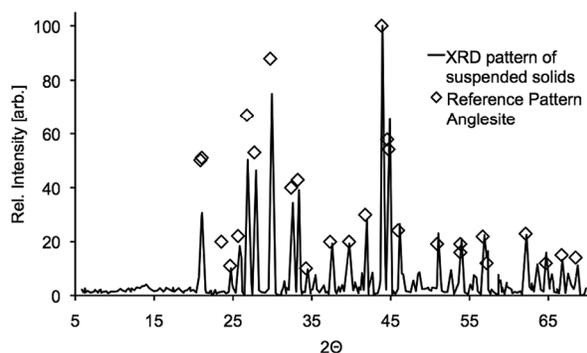
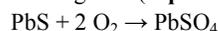


Figure 3: XRD pattern for the suspended solids from the weak acid sample.

A powder-X-ray diffraction pattern for the suspended solids is shown in **Figure 3**. The reflections fitted those of anglesite (PbSO₄, PDF FILE 00-036-1461) scoring 85% in the search and match option of the PANALYTICAL data processing software. This was in accordance with other findings where the anglesite was reported to form in the exhaust during the smelting of ore

containing lead (**Equation 3**).¹⁷



(**Equation 3**)

According to the elemental analysis the suspended solids were comprised to 64 ± 2 % w/w of lead. Anglesite has a lead content of 68.3 % w/w. The values appear to be agreeing well indicating that the suspended solids were comparatively pure anglesite, PbSO₄, particles.

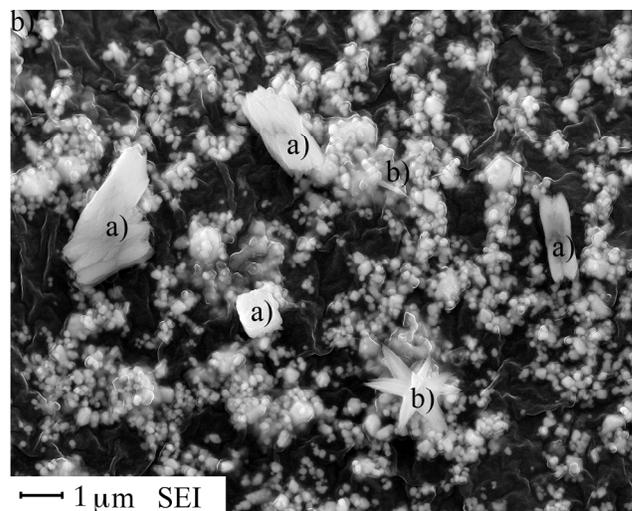


Figure 4: Three different types of structures observed in the suspended solids: a) rectangular rhomboids; b) star shapes; and unlabeled nanoparticles (bright, white dots and clusters of dots).

Some of the remaining reflections fitted compounds such as arsenic trioxide and iron sulfite. However, the score for the fit of these structures was very low even after subtraction of the anglesite pattern. They are likely to be due to impurities and compounds formed from the residual solution covering the suspended solids.

To confirm the results from the elemental analysis and the XRD and to assess the nature of the anglesite particles further a portion of the suspended solids was analyzed by electron microscopy. Scanning electron microscopy analysis revealed three types of solid structures. The largest structure observed was a rhomboid as shown in four spots (marked as a) in **Figure 4** in the secondary electron image of the dried suspended solids sample.

The particles marked with a) were composed mainly of sodium, sulfur and oxygen as shown by energy dispersive spectroscopy (EDS) and associated X-ray maps (**Figure 5**). The high correlation of the three elements represented as white in the convoluted representation (overlay) indicated that this structure probably is crystalline sodium sulfate. There was no evidence for crystals of sodium sulfate in the XRD pattern of the suspended solids. Considering the solubility of sodium sulfate, it was thought that these crystals formed during the drying step of sample preparation from the liquid films covering the suspended solids.

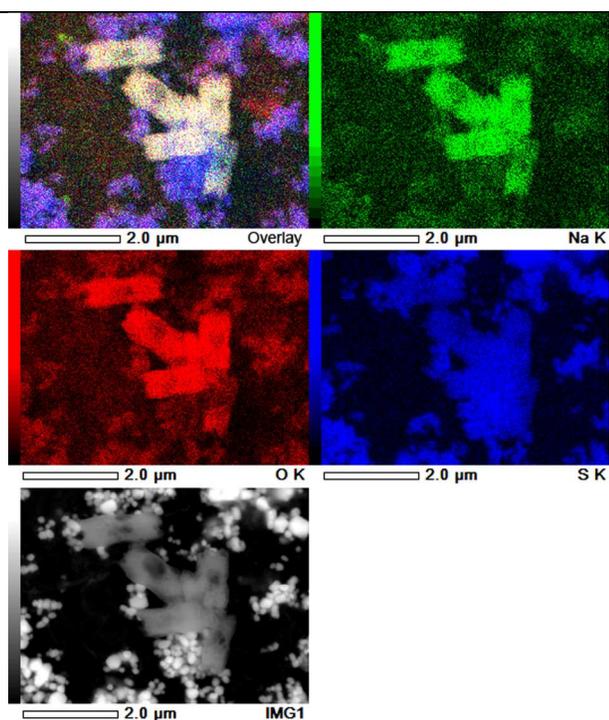


Figure 5: SEM-EDS analysis of the rhomboid type of structures found in the suspended solids. Presence of sulfur is shown in blue, oxygen in red and sodium in green. The overlay of oxygen and sulfur is represented as purple and the overlay of oxygen, sulfur and sodium as white. A backscattered electron image is presented in greyscale for orientation.

The second type of structure corresponded to a star shaped particle as shown in the spots marked as b) in **Figure 4**. It had a high content of arsenic, calcium and oxygen as evidenced by EDS. An X-ray overlay map produced using the EDS data is showing the structure in white colour in the convoluted representation in **Figure 6**, suggesting it to be a calcium arsenate crystal. This could not be corroborated by XRD, as a corresponding pattern of calcium arsenate was not observed. According to the elemental analysis calcium and arsenic could be considered impurities being only present at levels of about 0.1 to 0.2 % w/w. This is corroborated by the fact that the signal for arsenic is barely distinguishable from the background in the EDS. The star-shaped particles proved unstable and suffered irreversible damage during electron microscopy, which suggested that the particles might have lost water molecules from their lattice. Calcium arsenate was probably present in the suspended solids in amorphous form and only crystallized during sample preparation and analysis.

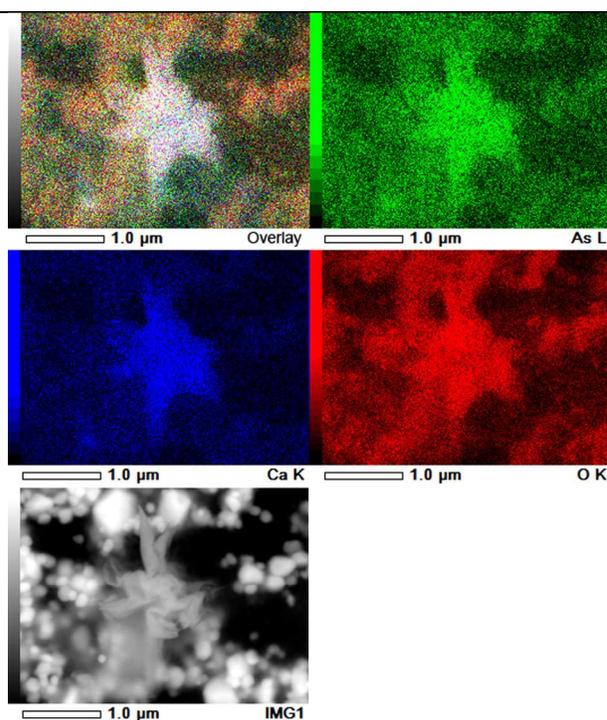


Figure 6: SEM-EDS imaging of the star shaped type of structures observed in the suspended solids. Presence of calcium is represented in blue, oxygen in red and arsenic in green. The overlay of these three elements is shown in white. A backscattered electron image is presented as well for orientation.

The third type of particles represents the predominant species found in the suspended solids. These particles were sized in the range from 50-500 nm. These nano- and microparticles are noticeable in **Figure 4** as bright, white dots and clusters of dots. Considering that commonly used microfiltration membranes in chemical analysis have a cut-off point of 0.45 µm, it was most likely that these particles bypassed any filtration and gas purification steps carried out in the sulfuric acid plant. It was also likely that some of these nanoparticles will have remained in the filtrate and, hence, contributed to the quantification of sulfate in solution during the analysis presented earlier. The analysis of the solution showed a lead concentration of 0.11 mol.L⁻¹. Considering the solubility of lead sulfate ($K_{sp} = 2.53 \cdot 10^{-8}$) and the high level of sulfate in solution it could be calculated that only about 0.07 mol.L⁻¹ lead should be present in solution. The remaining third of the lead was supposedly present in the form of nano- and microparticles, which remained suspended in the liquid even after allowing the suspended solids to settle and after filtration.

The images of the nanoparticles presented them in a strong contrast to the background, especially when the backscattered electron detector of the SEM was employed (**Figure 4**). This indicated either high density of the material or high atomic mass of the constituents. EDS analysis (**Figure 7**) suggested that the nanoparticles were mainly composed of lead, sulfur and oxygen. This confirmed the XRD results shown in **Figure 3** and elemental analysis of the suspended solids indicating strongly that the main component of the suspended solids of the weak acid is anglesite (PbSO₄). Moreover, the nanoparticles did not suffer structural changes during any of the analysis methods.

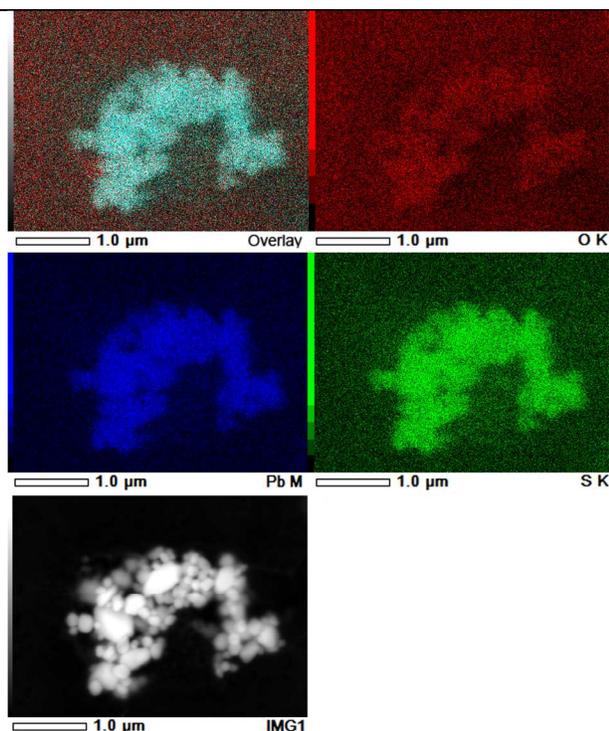


Figure 7: SEM-EDS imaging of the nanoparticles. Lead is represented as blue, oxygen as red and sulfur as green. The overlay of oxygen, sulfur and lead mapping is represented in light blue. A backscattered electron image is presented in greyscale for orientation.

Conclusions

The weak acid generated in two different scrubbers at El Teniente mine, in Chile, was composed of a liquid (supernatant) and solid phase (suspended solids). The supernatant contained a higher concentration of total arsenic than found in the weak acid of the Toyo (Japan) and Huelva (Spain) smelters. Sulfate concentrations were about half of those found in the weak acid of the Toyo smelter.⁶ These differences could be related to the lower metal sulfide and higher arsenic content in the ore being processed at El Teniente and that the samples studied here could be considered representative for similar smelters with sulfuric acid producing plants.^{6,15} Chemical analysis of the supernatant showed that it had a low pH-value of 0.45 and contained a concentration of copper (562 mg.L⁻¹) and molybdenum (50.3 mg.L⁻¹) that exceeded expectations by the plant engineers of El Teniente but was of the same order of magnitude as copper concentrations in the weak acid reported at other smelters. As the disposal of copper with the weak acid represents a considerable loss in commodities, copper is recovered using NaHS at the Toyo smelter. Taking into consideration the concentration of the different analytes the weak acid can be classified as an extremely acidic and high metal content waste using the Ficklin diagram.

Suspended solid concentrations showed large spikes on a few dates (where the upper action limit was exceeded), which contributed to a large value for the standard deviation for the solids concentrations. Average concentrations of suspended solids in the weak acid were 0.23 ± 0.63 % w/w for plant 1 and 0.97 ± 0.95 % w/w for plant 2 for the period from April to October 2010. Overall, both plants operated almost all of the time

within the control limits and exhibited very few concentration spikes over the studied period of time (**Figure 1 and 2**).

SEM, EDS, powder-XRD and ICP-OES analysis indicated strongly that the suspended solids found in weak acid waste were mainly comprised of anglesite (PbSO₄) nano- and microparticles. The findings of this study differ from those obtained by Morales et al. reporting on the flue dust coming from the flash smelting furnace of El Teniente.⁹ Morales et al. reported particles of a complex structure containing multiple mainly copper based minerals such as cuprospinel, chalcocyanite, dolerofanite, delafossite, zincosite, claudetite, arsenolite and tenorite. Furthermore, most particles found in the flue dust were two orders of magnitude larger than the ones present in El Teniente's weak acid presented here. Roca et al found that the particles contained a high concentration of copper that could be easily leached out with water. It is possible that the flue dust either didn't contain any anglesite or that the particles escaped collection due to their size. Further investigations are required to confirm either of these possibilities.

From an environmental and toxicological point of view the solid phase represents a serious hazard, not only due to its high concentration in lead but also due to the fact that it is composed of nanoparticles, which can bypass filters and easily become airborne as dust due to their small size. Romo-Kröger et al. found that especially wind erosion contributed to the spread of contaminants.³ Some of the smaller nanoparticles could be carried in the smoke and exhaust of the sulfuric acid producing plants. Even if the particles remain in the weak acid, it is possible that they become airborne at a later stage. Upon treatment of the weak acid some of these nanoparticles could be occluded inside the 'dirty gypsum' and be deposited at a landfill.^{16,18} If this is the case, it needs to be established if they could be dislodged by wind or water erosion from the 'dirty gypsum' and be leached into the environment. If the particles remain in the weak acid and are discharged into rivers, they could be taken up by aquatic life forms and end up in the food chain. It appears vital to establish the fate of the nanoparticles, as they are likely to pose health and environmental threats due to their toxicity and particle size.

Acknowledgements

The authors would like to acknowledge Comisión Nacional de Investigación Científica y Tecnológica (CONICYT, Chile) for financial support in form of a PhD scholarship. Further support was provided by the Faculty of Science and Engineering of Victoria University of Wellington and the Ministry for Science and Innovation. Special thanks go to staff of CODELCO, particularly to Victor Antonucci, who provided the samples and data. We thank CODELCO for allowing use of the data and our measurements in this publication.

Notes and references

- ^a School of Chemical and Physical Sciences, Victoria University of Wellington, New Zealand. E-mails: giancarlobarassi@gmail.com, martin.klimsa@web.de, aoc@gmx.li, mat.cairns@gmail.com
^{*} Present address: Othbergstr. 10, 37632 Eschershausen, Germany
^b Applied Chemistry, Georg-Simon-Ohm University, Nürnberg, Germany. Tel: ++49 911 5880 1540; E-mail: Joachim.Kinkel@ohm-hochschule.de

^c Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Chile. Tel: ++56 2978 1660 - 1619; E-mail: fvalenzu@uchile.cl

- 1 M.E. Schlesinger, M.E. Davenport, M.J. King, K.C. Sole, W.G. Davenport, *Extractive Metallurgy of Copper*, Elsevier Science, 2011.
- 2 C. M. Romo-Kröger, J. R. Morales, M. I. Dinator, F. Llona, L. C. Eaton, *Atmos. Environ.*, 1994, **28**, 705, DOI: 10.1016/1352-2310(94)90047-7.
- 3 C. M. Romo-Kröger, F. Llona, *Atmos. Environ Part A - Gen.*, 1993, **27**, 401, DOI: 10.1016/0960-1686(93)90114-E.
- 4 J. Newbold, *J. Clean. Prod.*, 2006, **14**, (3-4), 248, DOI: 10.1016/j.jclepro.2004.05.010.
- 5 G. Lagos, J. M. Lehuédé, M. Andia, *Resources Policy*, 2001, **27**, 147, DOI: 10.1016/S0301-4207(01)00015-0.
- 6 A. Ante, *Erzmetall*, 2005, **2**, 75.
- 7 A. Ante, S. Schonbrunner, *Zkg International*, 2007, **60**, 59.
- 8 CONAMA, Decreto Supremo n°90, online on http://www.siss.gob.cl/577/articles-4257_recurso_1.pdf, last accessed 28.7.2014.
- 9 A. Morales, M. Cruells, A. Roca, R. Bergó, *Hydrometallurgy*, 2010, **105**, 148, DOI: 10.1016/j.hydromet.2010.09.001.
- 10 C. Nunez, F. Espiell, A. Roca, *Hydrometallurgy*, 1985, **14**, 93, DOI: 10.1016/0304-386X(85)90069-6.
- 11 M. Czaplicka, L. Buzek, *Water Air Soil Pollut.*, 2011, **218**, 157, DOI: 10.1007/s11270-010-0631-6.
- 12 W.G. Davenport, M. King, A.K. Biswas, M. Schlesinger, *Extractive metallurgy of copper*, Pergamon Press, Oxford, England, 2002.
- 13 T. Inami, K. Baba, Y. Ojima, Clean and high productive operation at the Sumitomo Toyo smelter, in: *Sixth International Flash Smelting Congress*, Brazil, 1990.
- 14 D. Ivsic-Bajceta, Z. Kamberovic, J. Rogan, M. Cirkovic, T. Pavlovic, *Metall. Mater. Eng.*, 2013, **19** (3), 217, UDC: 628.161.2:546.561.
- 15 B. Lottermoser, *Mine wastes : characterization, treatment and environmental impacts*, 3rd ed., Springer, New York, 2010.
- 16 G. Barassi, Ph.D. Thesis, Victoria University, 2013, <http://researcharchive.vuw.ac.nz/handle/10063/2639>.
- 17 V. Ettler, Z. Johan, A. Baronnet, F. Jankovskya, C. Giller, M. Mihaljevic, O. Sebek, L. Strnad, A. Bezdicika, *Environ. Sci. Technol.*, 2005, **39**, 9309, DOI: 10.1021/es0509174.
- 18 T. Borrmann, M. J. Cairns, B. G. Anderson, W. Hoell, J. H. Johnston, *International Journal of Environmental and Waste Management*, 2005, **8** (3/4), 383.