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Prediction of metal discharges from sulphidic mine tailings covered with soil

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Abstract Future releases of metals from sulphidic mine tailings from the Adak enrichment plant in northern Sweden have been estimated using mathematical models. The initial objective of the study was to evaluate the effect of different soil-cover designs on the predicted metal releases from the deposit. During the coarse of the study, the potential importance of pH-buffering reactions and of the actual path of the weathering reactions were identified. In particular, it was found that the releases of arsenic could potentially be high under certain chemical conditions that can arise in a soil-covered deposit.

BACKGROUND

A study of the release of metals from mine tailings at the disused Adak enrichment plant in the central part of the province of Lapland in northern Sweden is presented. At the plant, which was in operation between 1945 and 1978, ore from three nearby mines has been processed to produce a concentrate of chalcopyrite. About 6×10^6 tonnes of tailings from the process have been disposed of in a deposit that covers an area of 475 000 m^2. The tailings have a sulphur content of about 5% and significant concentrations of iron, copper, zinc, cadmium and arsenic.

In contact with air, the sulphidic minerals in the tailings will weather as a consequence of oxidation by the atmospheric oxygen. A method which is becoming established to limit the rate of this weathering process is to cover the deposit with soil. The design of such a cover should be optimized such that it is kept water-saturated over the whole year in order to minimize oxygen transport through the cover and in order to avoid ponding as this could cause erosion inflicting on the durability of the cover. In the present study, the water and oxygen transport through the cover, the oxidation of the sulphides as well as the dissolution and migration of the metals in the tailings have been modelled in order to evaluate the effect of different cover designs. The present paper focusses on the chemical processes governing the sulphide oxidation, together with the consequent metal dissolution and migration. In particular, the potential roles of buffering minerals and selective metal dissolution will be highlighted. In order to define the boundary conditions for these processes, a brief presentation of the modelling of the water and oxygen transport through the cover is also made.

MODELLING SEQUENCE

In the first step, the water saturation of the cover and the water flow through the cover is modelled using an unsaturated flow model. In the present study, these calculations have been one-dimensional since this well describes the expected flow geometry in the deposit with its large and flat top surface. The input parameter data needed are the hydraulic conductivities of the modelled materials and their variation with the saturation, as well as the capillary pressure as a function of the saturation. The materials that have been studied as alternatives for the cover are a local moraine with a relatively high clay content, the local moraine mixed with 3% bentonite, and consolidated peat. The saturated hydraulic conductivity of these materials fall within the range 10^{-9} - $5x10^{-8}$ m s^{-1}. In the reference case presented in this paper, the local moraine with a conductivity of $5x10^{-8}$ m s^{-1} has been assumed. Climatic data in the form of monthly averages of precipitation have been taken from a nearby meterological observation station and monthly values of the net infiltration have been calculated. In order to be conservative, i.e. not to underestimate the risk for drying out of the cover during the summer, it has been assumed that all snow melts in March and that the ground never freezes during the winter. The resulting monthly net infiltration that was used in the model varies between 92 mm in March down to -61 mm (net evaporation) in June.

The oxygen transport through the cover is constituted by advective transport of oxygen that is dissolved in the infiltrating water and diffusive gas transport through the partly water-filled pores of the soil. It has been shown by Magnusson & Rasmuson (1983) that the diffusive transport predominates in most cases including a soil cover, but that advective transport can be significant at high water saturation in the cover. The model used for the oxygen transport, (Rasmuson & Collin, 1988), includes a semi-empirical method by Millington & Shearer (1971) to evaluate the oxygen diffusivity as a function of the calculated water saturation. The oxygen diffusivity in the soil decreases several orders of magnitude when the saturation goes from dry to wet. It is therefore important that the soil is kept near saturation in order to reduce the rate of oxidation of the tailings.

When oxygen enters the deposit it will react with the sulphur in the sulphidic minerals of the tailings, thus creating sulphate and hydrogen ions. In this process, metals can dissolve into the infiltrating water. The metal solubilities are generally governed by the solubilities of solid hydroxide and carbonate phases. The solubilities of these phases are sensitive to the pH of the solution and will for most metals increase when the solution is acidified. Some of the minerals in the tailings, e.g. calcite, will act to buffer the pH and thus counteract the potential metal solubility increase. The solubility of arsenic will - under reducing conditions - be lower in an acidic environment than at high pH. The solubilities of metals in the infiltrating water have been calculated from thermodynamic data assuming both buffered and unbuffered conditions. The calculations were performed with the PHREEQE code (Parkhurst *et al.*, 1980). The thermodynamic data base had been complemented by the authors for the purposes of the current study.

The dissolved metals have been assumed to follow the infiltrating water downward through the deposit. This transport has been evaluated using a model accounting for advection, dispersion and chemical retardation by sorption onto the solid phase. The sorption is characterized by a distribution coefficient, K_d, describing the ratio between the metal concentration on the solid phase to that in the solution. The distribution coefficient is known to be strongly dependent on the pH. Most metals will be more strongly sorbed at high pH than at low pH. For zinc, copper and cadmium, the distribution coefficient increases by almost three orders of magnitude when pH goes from 5 to 7 (Sandén, 1988). Arsenic, however, will under some conditions be very poorly sorbed at high pH (Xu, 1991). Under buffered conditions, all metals except arsenic have been assumed to be sorbed with a distribution coefficient of 0.001 m^3 kg^{-1}. For arsenic no sorption has been assumed to occur. Both these assumptions are conservative, i.e. they tend to underestimate the time needed for the metals to migrate through the repository. For unbuffered conditions, the sorption has been neglected for all metals.

As a complement to the transport modelling mentioned above, the model PHREEQM (Appelo *et al.*, 1990), describing the coupling between chemical speciation and transport has been applied. PHREEQM is an interactively coupled code that calculates the speciation of the transported components at each point in space and time. In this part of the project, it has been possible to study the effect of selective dissolution of certain metals on the concentrations in the water leaving the deposit.

The results from the transport modelling are the time-dependent fluxes of metals across the bottom of the deposit. It has not been within the scope of the present study to model the further transport in the geosphere and the biosphere/recipient.

WATER AND OXYGEN TRANSPORT IN THE SOIL COVER

Six different designs of the soil cover have been evaluated within the project. They all involve a two-layered cover with a low-permeability layer covered by a protective layer consisting of a more permeable material. In the reference case forming the basis of the presentation in this paper, the low-permeability layer is constituted by a 0.5 m thick layer of a clayish moraine available from the vicinity of the site. This moraine is covered by a 1.5 m thick protective layer consisting of material which is locally found. Based on measurements on the actual material, the hydraulic conductivity has been assumed to be 5×10^{-8} m s^{-1} for the moraine and 1×10^{-7} m s^{-1} for the protective layer.

According to the calculations, the amount of infiltrating water is 170 mm $year^{-1}$ and the resulting rate of oxygen transport through the cover is 0.2 mol m^{-2} $year^{-1}$. In the tight moraine layer, the saturation is above 85% during the whole year. This is important in order to limit the rate of oxygen transport. The saturation is at its highest after the snow melt in March/April and after the autumn rains in November/December. During the end of the spring and the summer, the saturation decreases to reach a minimum in July-September. The resulting temporal variation of water infiltration and oxygen transport are shown in Fig. 1.

SULPHIDE OXIDATION AND METAL DISSOLUTION

The solubilities of iron, zinc, cadmium, copper and arsenic in the water have been calculated assuming thermodynamic equilibrium. The solubilities have been calculated for unbuffered, buffered and partially buffered conditions. The term buffered conditions in this context means buffered by calcite. The content of calcite in the tailings varies in the range 0.01-0.81% with an estimated average of 0.35% (Qvarfort, 1989). This amount of calcite is less than what

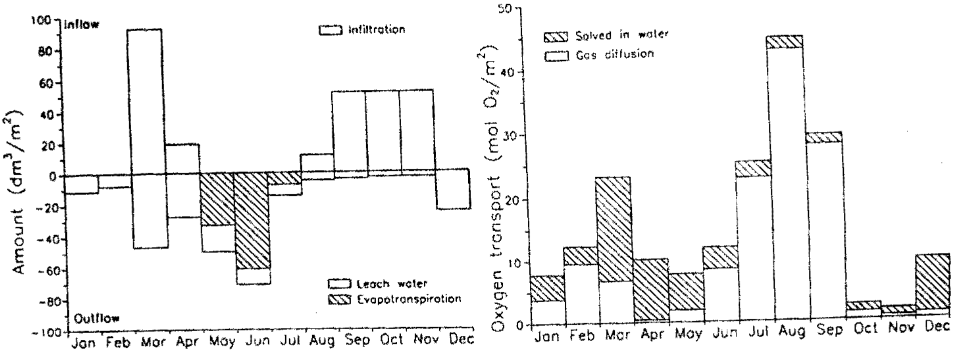

Fig. 1 Distribution of the calculated water infiltration (left) and oxygen transport (right). The values are given as monthly averages.

would be required to neutralize the maximum amount of acid that could be formed by oxidation of the sulphide.

The term partially buffered refers to buffering by different siliceous minerals such as biotite, cordierite, sodium-calcium feldspars, enstatite, diopside, amfibioles, chlorite, etc., that are abundant in the tailings. The buffering reactions of these siliceous minerals are known to be slower than the calcite buffering. It is therefore not certain that they will be effective during the relatively rapid oxidation during the period before covering the deposit. It is however quite possible that, when the rate of infiltration and the consequent rate of sulphide oxidation is brought down by the application of the soil cover, some of these minerals undergo weathering, thereby contributing to the buffering. If this sequence of processes takes place, the utility of the soil cover could be concluded to be twofold namely (i) reduction of the rate of weathering of sulphidic minerals and (ii) reduction of the metal solubilities by making the weathering reactions of the siliceous minerals more effective for pH-buffering. In the calculations, partial buffering by diopside, a calcium-magnesium silicate, has been assumed.

In the case of unbuffered conditions, neither calcite nor siliceous minerals are assumed to be effective as buffering minerals. The hydrogen ions created in the oxidation of the sulphide will therefore create a strongly acidic water with high metal concentrations leading to higher metal releases than in the case of effective buffering.

The solubilities calculated for the different degrees of buffering are shown in Table 1. The table clearly shows that buffering will lower the solubilities for iron, zinc and cadmium significantly, whereas the solubility of arsenic is higher under buffered conditions. The copper solubility is very low both for buffered and unbuffered conditions. As a variation, a case when only chalcopyrite is assumed to be oxidized has been calculated resulting in a copper solubility of $2.8\mathrm{x}10^{-4}$ mol l^{-1} for both buffered and unbuffered conditions.

The issue whether buffering will be effective or not is obviously of great importance. The availability of the buffering minerals to weathering is known to be affected by physical properties such as grain size, embedding of mineral grains in inert minerals, precipitation of for example iron hydroxides on the surface of the grains, etc. In order to investigate the tendency of the mine

Table 1 Solubilities (mol l^{-1}) calculated by PHREEQE and used as source concentrations in the advection-dispersion model for different assumptions regarding the buffering.

	Unbuffered	Partially buffered	Buffered
Fe	6.4×10^{-5}	2.6×10^{-6}	4.2×10^{-7}
Zn	4.2×10^{-4}	6.6×10^{-9}	1.2×10^{-9}
Cd	1.1×10^{-6}	$<10^{-10}$	$<10^{-10}$
Cu	$<10^{-10}$	$<10^{-10}$	$<10^{-10}$
As	1.4×10^{-7}	3.6×10^{-4}	3.5×10^{-4}

tailings at Adak to undergo buffering reactions, experiments were carried out at the National Geotechnical Institute in Linköping. Samples of tailings were mixed with controlled amounts of sulphuric acid under non-oxic conditions and the pH was measured. Preliminary results show that fast buffering reactions do take place indicating that calcite buffering might be effective. Buffering could even be observed when sulphuric acid corresponding to the theoretically maximum amount created by total weathering of the tailings was added. As this amount of sulphuric acid is greater than the theoretical buffering capacity of the calcite, buffering by weathering of siliceous minerals is likely to occur in this case. This is also supported by the fact that the buffering appears to be significantly slower in this sample than in the samples with less sulphuric acid. It was concluded that further studies of the buffering reactions in mine tailings would be worthwhile in order to improve the basis for making forecasts of metal discharges from deposits.

In the metal release calculations reported in the next section, buffered and unbuffered conditions have been assumed. No calculations were performed for partially buffered conditions because of uncertainties regarding the effectiveness of the weathering of siliceous minerals.

METAL RELEASES

The migration of dissolved metals downward through the deposit has been modelled using an advection-dispersion model and a coupled geochemical transport model as described above. Both model types should be expected to yield constant discharge rates over a prolonged period of time. This is because the time for migration through the 10 m thick deposit is relatively short (tens to a hundred years), compared to the time for complete depletion of leachable metals in the deposit (thousands to more than 10^5 years).

In the advection-dispersion model, the steady-state discharge rate is governed by the solubility of the metal as given in Table 1. Once the metals have dissolved they are only affected by sorption. Hence, this type of model does not account for reprecipitation of migrating metals, for example by contact with sulphidic minerals during the migration. Such processes are accounted for in the coupled model. The coupled model therefore gives a series of rates defined by the selective dissolution and depletion of specific minerals. A consequence of this is that the calculated discharge rates can be higher for certain time periods in the coupled model compared to those in the advection-dispersion model.

Advection-dispersion model

Figures 2 and 3 show breakthrough curves calculated with the advection dispersion model for iron, zinc, cadmium, copper and arsenic for buffered and unbuffered conditions. The calculations do not account for depletion as the metals are leached. This would influence the shape of the curve for cadmium in Fig. 2. With the calculated rate of migration the amount of cadmium available in the deposit would last only about 15 years. The inventory of other metals is sufficiently large to last for thousands of years, i.e. far beyond the time scales shown in Figs 2 and 3. In the case of buffered conditions the time for depletion is more than 100 000 years for all metals, except arsenic (<30 000 years).

When buffered conditions are assumed, the calculated discharge rates for iron, zinc and cadmium are several orders of magnitude lower than for unbuffered conditions, whereas the arsenic discharge rate is about three orders of magnitude higher due to the increase of solubility mentioned in the previous

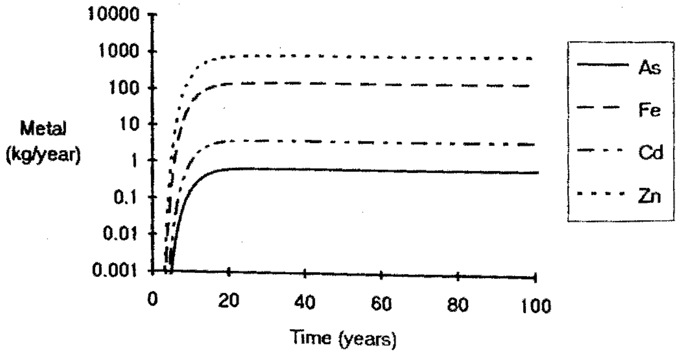

Fig. 2 Calculated breakthrough curves for discharge rates for unbuffered conditions (advection-dispersion model). Cu discharge is $<10^{-3}$ kg year^{-1}.

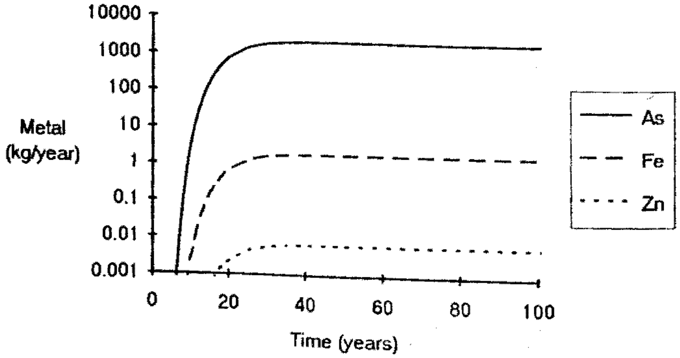

Fig. 3 Calculated breakthrough curves for discharge rates for buffered conditions (advection-dispersion model). Cu and Cd discharges are $<10^{-3}$ kg year^{-1}.

section. The results further underline that the issue of the effectiveness of buffering is of great importance in the forecasting of metal discharges.

The calculated discharge rates for copper are extremely low both for buffered and for unbuffered conditions due to the low solubility of chalcopyrite in the presence of other sulphide minerals. If chalcopyrite were the only sulphidic mineral available for weathering, the calculated release rate for copper would be 1440 kg year^{-1}. This underlines that experimental studies are necessary in order to clarify the reaction path of the weathering of tailings when several sulphides are present.

Coupled model

In the coupled model, chemical transitions as well as the migration of reactants and reaction products are calculated simultaneously. In the present calculations the process of oxidation and dissolution of pyrite, zinc sulphide, cadmium sulphide, chalcopyrite and arsenopyrite have been accounted for as well as the reprecipitation of secondary sulphides such as orpiment, $As_2S_3(s)$. The calculations have been made both for buffered and unbuffered conditions. Only a limited number of calculations were performed with the coupled model and the results from the calculations should only be seen as indicative of the processes and concentration levels that can be expected.

Table 2 shows schematically for a soil-covered deposit with initially calcite-buffered tailings the sequence of chemical processes that in the modelling were found to occur when oxygen and water penetrate through the cover into the deposited tailings. In the first two stages, the pH is kept relatively high: first due to weathering of the calcite content and later due to the dissolution of arsenopyrite ($FeAsS(s)$) and reprecipitation of arsenic as orpiment ($As_2S_3(s)$). When the calcite has been depleted and the arsenic has been transformed into orpiment, the pH drops to about 4 and dissolution of the zinc and cadmium sulphides starts. The last three stages involve dissolution of pyrite, orpiment and chalcopyrite respectively. During this final part of the weathering process the pH will drop to about 3. For unbuffered conditions the two initial stages of the sequence (calcite weathering and transformation of arsenopyrite) will not take place. The sequence for unbuffered conditions is thus similar to the last five stages in Table 2.

Table 2 Calculated metal concentrations (mol l^{-1}) for different stages in the sequence of reactions during weathering. Results for initially buffered conditions obtained by the coupled model.

Stage	pH	Fe	Zn	Cd	Cu	As
I	8.6	1.6×10^{-4}	1.0×10^{-9}	$<10^{-10}$	$<10^{-10}$	1.1×10^{-3}
II	7.8	1.7×10^{-4}	2.0×10^{-9}	$<10^{-10}$	$<10^{-10}$	1.1×10^{-3}
III	4	5.4×10^{-5}	3.5×10^{-4}	9.6×10^{-7}	$<10^{-10}$	1.3×10^{-7}
IV	4	5.4×10^{-5}	3.5×10^{-4}	-	$<10^{-10}$	1.3×10^{-7}
V	3.3	2.5×10^{-4}	-	-	$<10^{-10}$	7.6×10^{-8}
VI	3.1	-	-	-	$<10^{-10}$	3.10^{-4}
VII	3	-	-	-	2.8×10^{-4}	-

A comparison between Tables 1 and 2 shows that the coupled model yields higher solubilities for most metals - at least during some stage of the weathering sequence - than what is obtained from the speciation modelling of a stationary system. In the stationary model, the reaction products from weathering processes stay in the system and suppress the solubilities of less readily weathered sulphides. In the coupled model, the weathered components are dissolved and transported out of the system. When the readily weathered sulphides have been thus depleted the suppression mechanism is no longer available and result in a higher concentration of the less readily weathered sulphides. For copper, a solubility of $<10^{-10}$ mol l^{-1} was calculated with the stationary model whereas the coupled model yielded 2.8×10^{-4} mol l^{-1} at a very late time when all other sulphides had been depleted. This solubility is the same as that obtained in the stationary model assuming chalcopyrite is the only sulphide available.

Due to the toxicity of arsenic the arsenic concentration in the water exiting the deposit is of particular interest. It is therefore worth noting that the calculated concentration of arsenic is high during the initial calcite-buffered period and during stage VI when pyrite has been depleted. The chemical behaviour of arsenic is complex. In the present study, only a limited set of reactions has been included. Thus, for example, no reactions including arsenites or arsenides have been included. Metal compounds with these ions could potentially contribute to lowering the solubility of arsenic either in the deposit or in the groundwater below the deposit. The reactions that lead to the behaviour observed in the model are discussed below.

One main point in the discussion of the arsenic behaviour is whether the data used gives a representative picture of the solubility of arsenopyrite and orpiment. In the groundwater, the soluble arsenic is normally predominated by $H_3AsO_3(aq)$. In a reducing environment, like in a soil covered deposit, the solubility can be expected to be controlled by $As_2S_3(s)$, Eary (1992). Thermodynamic data vary within a wide range. Eary (1992) gives data for ΔG^0_f that vary between -168.8 and -95.4 kJ mol^{-1}. Measurements of the solubility of amorphous $As_2S_3(s)$ yielded $10^{-3.5}$ mol l^{-1} at pH<7. This value is comparable to the results from the coupled model for reducing conditions and low pH. For acidic conditions the dissolution and precipitation of $As_2S_3(s)$ occurs according to:

$$As_2S_3(s) + 6\,H_2O \Leftrightarrow 2\,H_3AsO_3 + 3\,H_2S$$

At pH<7, the H_2S is stable and the solubility of the $As_2S_3(s)$ independent of the pH. At higher pH H_2S is dissociated leading to a sharp increase in arsenic solubility. The reaction can then be described by:

$$As_2S_3\,(s) + 3\,H_2O + 3\,OH^- \Leftrightarrow 2\,H_3AsO_3 + 3\,HS^-$$

For amorphous $As_2S_3(s)$ the solubility at pH 8 has been measured to be 10^{-2} mol l^{-1}, Eary (1992), and for the crystalline $As_2S_3(s)$ to be $10^{-3.2}$ mol l^{-1}, Webster (1990). These values can be compared with the $10^{-2.96}$ mol l^{-1} obtained at pH=7.8-8.6 in the coupled model.

The solubility of $As_2S_3(s)$ can be suppressed by the supply of hydrogen sulphide from the dissolution of some of the other metal sulphides present, e.g. zinc sulphide. The solubility has a minimum at about 10^{-6} mol l^{-1} at a sulphide concentration between 10^{-4} and 10^{-3} mol l^{-1} (Eary, 1992; Webster, 1990). This behaviour can be observed in the coupled model where a solubility of $10^{-6.9}$ mol l^{-1} was obtained at a sulphide concentration of about 10^{-4} mol l^{-1}. At higher sulphide concentrations, the solubility of $As_2S_3(s)$ increases due to the formation of soluble poly-sulphide complexes (Eary, 1992; Webster, 1990).

It should be noted that no precipitation of ferric hydroxides is observed in the calculations. In fact, it has been discussed in other contexts that ferric hydroxide could contribute to the oxidation of sulphides after the decrease of oxygen supply from the atmosphere by the application of the soil cover. The calculated water composition indicates, however, that ferric hydroxide could be precipitated when the water leaves the deposit and is mixed with surface waters. This could possibly suppress the arsenic concentrations in the recipient by the formation of ferric arsenate. This has not been investigated in the present study.

CONCLUSIONS

The release of metals from a deposit for sulphidic mine tailings has been studied by model calculations. As expected, the calculations have shown that the soil cover is efficient for bringing down the rate of oxygen transport into the deposit and the consequent rate of weathering of the sulphidic minerals. This leads to lowering of the discharges of several metals such as copper and zinc. There are indications that both calcite and some siliceous minerals in the tailings could buffer the pH to the range 7-9. If it could be convincingly shown that these buffering reactions are effective, it would contribute to increasing the credibility of the analysis of the effects of soil covering as a means for remediation of deposits for sulphidic mine tailings.

In the study, a so-called coupled chemistry and transport model has been applied to estimate the releases from the deposit. This type of model accounts for the simultaneous interaction between different chemical transformations, and also describes the transport of reactants and reaction products. The results of the coupled model show higher releases during certain periods compared to the results of a classical transport model where all metals dissolve simultaneously in the source. The results, although yet only indicative, clearly demonstrate the utility of applying this type of model to assess the future environmental consequences.

Arsenic shows a somewhat different behaviour than the other metals studied. The calculated solubility of arsenic is high under reducing conditions and high pH when the solubilities of the other metals are low. There are even indications that the covering of the deposit might create such chemical conditions that the arsenic discharges become higher than they would have been if the deposit were to be left uncovered. Further studies might shed light on the effects of such reactions that have been omitted in the present project. For example, a reaction between ferric hydroxide and arsenates or the formation of metal arsenides might contribute to limiting the arsenic discharges.

None of the models used in this study accounts for the kinetics of the different weathering reactions. It is therefore possible that some of the anticipated reactions do not occur in the real system because of slow kinetics. If the weathering of one metal sulphide is kinetically hindered, this could lead to an increase of the release from other metal sulphides. Further study of these issues would increase the credibility of the analysis.

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