Article

Removal of Metals by Sulphide Precipitation Using Na$_2$S and HS$^-$-Solution

Hanna Prokkola *, Emma-Tuulia Nurmesniemi and Ulla Lassi

Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland; emma-tuulia.nurmesniemi@oulu.fi (E.-T.N.); ulla.lassi@oulu.fi (U.L.)

* Correspondence: hanna.prokkola@oulu.fi; Tel.: +358-50-4288295

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Abstract: Precipitation of metals as metal sulphides is a practical way to recover metals from mine water. Sulphide precipitation is useful since many metals are very sparingly soluble as sulphides. Precipitation is also pH dependent. This article investigates the precipitation of metals individually as sulphides and assesses which metals are precipitated as metal hydroxides by adjustment of the pH. The precipitation of different metals as sulphides was studied to determine the conditions under which the HS$^-$ solution from the sulphate reduction reaction could be used for precipitation. H$_2$S gas and ionic HS$^-$ produced during anaerobic treatment could be recycled from the process to precipitate metals in acidic mine drainage (AMD) prior to anaerobic treatment (Biological sulphate reduction), thereby recovering several metals. Precipitation of metals with HS$^-$ was fast and produced fine precipitates. The pH of acid mine water is about 2–4, and it can be adjusted to pH 5.5 before sulphide precipitation, while the precipitation, on the other hand, requires a sulphide solution with pH at 8 and the sulphide in HS$^-$ form. This prevents H$_2$S formation and mitigates the risk posed from the evaporation of toxic hydrogen sulphur gas. This is a lower increase than is required for hydroxide precipitation, in which pH is typically raised to approximately nine. After precipitation, metal concentrations ranged from 1 to 30 µg/L.

Keywords: acid mine drainage; precipitation; metal sulphides; metal hydroxides

1. Introduction

Access to potable water is not universal. Only 3% of the Earth’s water is fresh water and, therefore, the contamination of existing water supplies is a problem of global significance. The main sources of water contamination are mine water, leachate, municipal wastewater, and urban runoff. Industrial wastewater also pollutes water supplies and metals are among the most common contaminants contained in this wastewater [1]. Metal ion pollution is highly persistent. Many metals are toxic at high concentrations especially under uncontrolled release into the environment when the natural background values are exceeded. The exposure is mainly caused by inhalation, dermal contact, and ingestion. The presence of various metals, such as Cr, Pb, Zn, As, Cu, Ni, Co, Cd, and Hg, causes disturbances in circulatory, gastrointestinal, and nervous systems. They can also affect various organs, including the central nervous system, leading to mental disorders, and damage the blood constituents, which may result in damage to the lungs, liver, kidneys and other vital organs, promoting several disease conditions [2] and possibly leading to blindness, deafness, brain damage, loss of fertility, cancer, and many other severe health problems that may ultimately be fatal [3].

Acidic mine water that contains sulphates and metal ions is formed as a waste product of the mining and mineral industry. Biological sulphate reduction could be used as an inexpensive and effective way to purify waters with a high sulfate content but needs further investigation. Conventionally, metal-containing wastewater is neutralized with an alkali, such as calcium carbonate.
or calcium oxide/calcium hydroxide, in order to precipitate metals as hydroxides [4]. Metals precipitate as hydroxides according to their specific pH values (Figures S1–S15). Chemical treatment with alkalis has high operating and maintenance costs and produces large volumes of sludge that require disposal [5]. Still, the treatment of acidic mine drainage AMD with lime is the most common technology in industrial scale for cost reasons and the lack of cheap economic alternatives. The disadvantages of hydroxide precipitation include relatively high residual concentrations of metals in wastewater (0.5–2 mg/L), disruption of chelating agents, and inappropriate re-use of sludge in the presence of several metals.

Sulphide precipitation is an alternative that helps to achieve very low residual metal concentrations (<0.01 mg/L) and experiences interference from chelating agents. The final concentration of sulphide precipitation is related to pH (Figure 1) and the process is much more efficient than hydroxide precipitation. As can be seen from Figure 1, the solubility of sulphides is considerably lower than that of hydroxides, and they are also acid soluble. Importantly, metal recovery is possible using sulphide precipitation as some metals can be precipitated separately when adjusting the pH stepwise [6]. Table 1 shows that most transition metal sulfides are highly insoluble (CdS, FeS, and ZnS). Sulphides of lead are sparingly soluble. Most hydroxides are only slightly soluble.

![Figure 1. Precipitation pH and concentrations of hydroxides and sulphides.](image-url)
Table 1. Theoretical values for metal sulphide and hydroxide precipitation [7].

| Metal | Solubility Product Metal Sulphide (log $K_{sp}$) | Solubility Product Metal Hydroxide (log $K_{sp}$) |
|-------|-----------------------------------------------|-----------------------------------------------|
| Zn    | −24.5                                        | −16.1                                        |
| Co    | −22.1                                        | −14.5                                        |
| Ni    | −21.0                                        | −15.3                                        |
| Fe    | −                                             | −38.6                                        |
| Fe(II)| −18.8                                        | −16.3                                        |
| Mn    | −13.3                                        | −12.7                                        |
| Ag    | −49.2                                        | −7.9                                         |
| Cd    | −28.9                                        | −14.3                                        |
| Co    | −22.9                                        | −14.5                                        |
| Cu    | −35.9                                        | −19.8                                        |
| Hg    | −52.2                                        | −25.4                                        |
| Pb    | −28.1                                        | −19.9                                        |
| Sn    | −27.5                                        | −26.3                                        |

Different sources provide different information on the pH range of sulphide precipitation for metals; Table 2 shows the lowest pH range where the metal sulphide salts are still in a soluble form [8]. Sulphide precipitation can be carried out using either solid (FeS, CaS, and Na$_2$S), aqueous solutions (Na$_2$S, NaHS, and NH$_4$S) or, most commonly, gaseous sulphide sources (H$_2$S) [8,9]. In order to improve the techno–economic conditions, the result of the purification of metals can be improved by precipitating them using a hydrogen sulphide solution (HS$^-$). It is produced during biological sulphur reduction instead of using the hydrogen sulphide gas described in [10]. The use of highly toxic hydrogen sulphide gas in the precipitation of metals as metal sulphide could be replaced by converting it to soluble H$_2$S or solid Na$_2$S. One aspect of sustainable development to reduce environmental impact is both metal recovery and recycling. The ionic HS$^-$ produced in the anaerobic process and recycled to precipitate metals from acidic wastewater prior to anaerobic treatment and thus to recover various metals is under study in many cases. This could improve material efficiency in wastewater treatment.

Table 2. Theoretical pH values for metal sulphide precipitation [11,12].

| Metal Sulphide | Precipitation pH $^1$ | Precipitation pH $^2$ |
|----------------|-----------------------|-----------------------|
| CuS            | 2.5                   | 1.5–2                 |
| ZnS            | 5.5                   | 2.2–4.1               |
| CdS            | 4                     |                       |
| CoS            |                       | 4.5–5.8               |
| NiS            | 7.5                   | 5.6–8.6               |
| FeS            |                       | 5–7.4                 |
| MnS            |                       | 7.7–9.7               |

$^1$ Gharabaghi. $^2$ Nevatalo.

The precipitation of metals by HS$^-$ is rapid but requires pH adjustment. The precipitation of metals as sulphides usually occurs at lower pH values than the precipitation of metals as hydroxides, although the pH must not be too low, as some sulphide precipitates are acid soluble. Although it is necessary to adjust the pH during the precipitation of metals as sulphides, the required pH adjustment is smaller, which leads to a reduction in the use of lime and, consequently, lowers costs. pH adjustment is necessary if water from the sulfate reduction reaction is recycled to metal precipitation. In this case, when the pH is too low, a situation arises in which hydrogen sulphide is converted into H$_2$S gas and the pH of the anaerobic is lowered, which is undesirable. It is noteworthy that lime is a virgin resource with a limited availability. The pH can also be adjusted with NaOH [13]. Metal sulphide precipitates are acid soluble; therefore, the pH of the solution to be precipitated must be adjusted above five, except for example HgS and CdS, which can precipitate at very low pH. The metals studied in this article
precipitated when the pH was raised above five. At lower pH values, precipitation was not studied. Both HS\(^{-}\) and Na\(_2\)S were used in this study of sulphide precipitation of metals. Additions were made both as solid and as solution. The purpose of the study was to investigate sulphide precipitation in a solution with several metals.

2. Theory

Hydrogen sulphide is formed by reducing sulphate in a biological sulphate reduction by reaction with a carbon source according to Equation (1).

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^{-} \tag{1}
\]

From the reaction equation, it can be seen that 1 mol of sulphate consumes 2 mols of carbon and produces 1 mol of hydrogen sulphide.

Metals precipitate as sparingly soluble sulphides at specific pH values according to Equations (2) and (3) [5].

\[
\text{M}^{2+} + \text{S}^{2-} \leftrightarrow \text{MS(s)} \tag{2}
\]

\[
\text{M}^{2+} + \text{HS}^{-} \leftrightarrow \text{MS(s)} + \text{H}^{+} \tag{3}
\]

In a saturated solution (Equation (3)) formed by precipitation, both dissolution and precipitation occur simultaneously. This is when the system is in equilibrium. Equations (4)–(6) show the dissolution of salt at equilibrium in water and the solubility product. In a general way for an electrolyte that dissolves in water according to the reaction [14].

\[
\text{A}_m\text{B}_n (s) \leftrightarrow m\text{A}^{+n} (aq) + n\text{B}^{-m} (aq) \tag{4}
\]

The equilibrium condition is:

\[
\{\text{AmBn(s)}\} = \{\text{A}^{+n} (aq)\}^m \{\text{B}^{-m} (aq)\}^n \tag{5}
\]

The conventional solubility expression:

\[
K_{s0} = \{\text{A}^{+n} (aq)\}^m\{\text{B}^{-m}(aq)\}^n \tag{6}
\]

Figure 2 shows the Eh-pH diagram of hydrolysis speciation of sulphide and sulphate. The presence of hydrogen sulphide (HS\(^{-}\)) in the solution is pH dependent, occurring between pH 7–13. Hydrogen sulphide is a highly water-soluble gas (4–6 g/L) and can exist in solution in three different forms (i.e., H\(_2\)S, HS\(^{-}\), or S\(^{2-}\)) depending on the Eh-pH conditions. If precipitation is not desired with gaseous hydrogen sulphide, the alternative is to use a solution that has a pH of about eight, wherein the hydrogen sulphide is in the form of HS\(^{-}\) or else the pH of the biological sulphate reduction reaction mixture should be adjusted to 7–8 because this is optimal for sulphate reduction. Of course, precipitation can be carried out at a lower pH, but then some hydrogen sulphide will evaporate, which is undesirable. If the pH > 7, soluble sulphide could be used for precipitation, thus avoiding the use of toxic gaseous hydrogen sulphide.
Precipitation of different metals from solution was done at pH 8 and 11.6. If HS\textsuperscript{−} is used for precipitation under neutral conditions, a pH of between 7–8 is used. The cost of pH adjustment using this method is still less than the costs of lime precipitation, where pH 9 is typically used. The study found that hydrogen sulphide-containing water obtained from biological sulphur reduction can be used for metal precipitation, in which case the pH of the metal solution only needs to be adjusted to 5.5.

Precipitates can be separated under laboratory conditions by centrifuging. Sedimentation succeeds in these experiments, but the process may take a couple of days. On a larger scale, sedimentation is a good option since the precipitate is quite heavy compared to hydroxides. Filtration does not work for all the precipitates; there are fine precipitates that go through a small filter paper (0.45 µm) or sinter only to color it. The crystallization of the precipitate is rapid, and therefore the precipitates are finely divided.

3. Materials and Methods

Sulphide precipitation of the following metal salts was studied: MnSO\textsubscript{4}·H\textsubscript{2}O, Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·18H\textsubscript{2}O, MgSO\textsubscript{4}·7H\textsubscript{2}O, Zn acetate, Sr(NO\textsubscript{3})\textsubscript{2}, CoCl\textsubscript{2}, NiSO\textsubscript{4}·6H\textsubscript{2}O, SbCl\textsubscript{3}, SnCl\textsubscript{2}, FeSO\textsubscript{4}·7H\textsubscript{2}O, CuSO\textsubscript{4}·5H\textsubscript{2}O, Pb(NO\textsubscript{3})\textsubscript{2}, Hg(NO\textsubscript{3})\textsubscript{2}, Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O, and CdSO\textsubscript{4}. Different sediments were prepared for this purpose. The measurements of metal concentrations were performed in an accredited laboratory and in accordance with the standard SFS-EN ISO 17294-2:2016. Precipitation was performed with both solid Na\textsubscript{2}S and HS\textsuperscript{−} solution. The aqueous Na\textsubscript{2}S solution has a pH of about 11.6. The pH of this solution was adjusted to eight. The pH of the metal solution was initially about 5.5. The reaction vessels were one liter decks with slow magnetic stirring. Samples were taken after 20 h when all the precipitate had settled. The precipitate was separated by filtration after it was settled. Some had to wait two or three days so that the crystal size grew large enough for filtration. The deposition of these was not specific to a particular metal. Solid Na\textsubscript{2}S was added in excess to make sure everything precipitated. In the precipitation solution (Na\textsubscript{2}S), the sulphur concentration was 0.49 g/L (2 g/L 60%). The pH was adjusted to 8. Eh-pH diagrams were calculated using HSC Chemistry version 9. Analysis of precipitates was done using PANanalytical X-ray diffraction (XRD) equipment with Cu K\textalpha at 40 mA and 45 kV. Metal analysis of water samples was done by ICP-OES using standard SFS-EN ISO 17294-2:2016 at accredited laboratory.
4. Results and Discussion

4.1. Sulphide Precipitation Using Solid Na$_2$S

Precipitation using a Na$_2$S solution with a pH of 11.6 resulted in the same amount of metal removal regardless of the pH of the starting solution to be precipitated. The pH of the solutions to be precipitated were 2, 6, and 10. The final concentrations were all, with some exceptions, below 0.075 mg/L (Table 3). As can be seen from Table 3, although the output pH was very low (i.e., 2), precipitation still occurred because the solid reagent increased the final pH. After adjusting the pH, precipitates after the hydroxide precipitation could be recovered, but this step could be avoided by collecting all the precipitates after the subsequent hydrogen sulphide precipitation. However, not all metals precipitated as hydroxides were recovered at this stage because their solubility yields were higher than those of the sulphide precipitates. Table 3 shows how metals were precipitated in the experiments where solid Na$_2$S was used as the precipitant. The starting pH had little effect because solid Na$_2$S raised the pH so much that precipitation occurred. The metals were precipitated both separately and together. Table 3 shows the results obtained by precipitating a solution of uniform pH with solid Na$_2$S. In practice, it can be difficult to dispense a solid reagent, although it is a good precipitator. This problem was overcome when using a HS- solution.

Table 3. Precipitation of some selected metals with Na$_2$S.

| Metal | Initial Metal Concentration [mg/L] | Concentration after Precipitation pH 2 [mg/L] | Concentration after Precipitation pH 6 [mg/L] | Concentration after Precipitation pH 10 [mg/L] |
|-------|----------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Co    | 31.9                             | <0.015                                        | <0.015                                        | <0.015                                        |
| Cu    | 51.0                             | <0.025                                        | <0.025                                        | <0.025                                        |
| Fe    | 30.4                             | <0.075                                        | <0.075                                        | <0.075                                        |
| Mg    | 28.8                             | 0.46                                          | <0.13                                         | <0.13                                         |
| Mn    | 48.6                             | <0.025                                        | <0.025                                        | <0.025                                        |
| Sr    | 90.7                             | 32.8                                          | 0.37                                          | 0.72                                          |
| Zn    | 36.4                             | <0.050                                        | <0.050                                        | <0.050                                        |

4.2. Sulphide Precipitation Using Na$_2$S Solution

Many metals were precipitated when using a solution of Na$_2$S with a pH above 11 for precipitation. These results were not measured separately as sulphides and hydroxides. Dosage of reagent as solution may be easier because it will cause lesser variation of pH values. Some metals precipitate as hydroxides, and since sulphide is in the HS- form above pH 7, it can be used for precipitation without fear of evaporating gaseous sulphide. Some metal sulphides are also soluble in bases, so the pH should not be too high. [6]

Table 4 shows which metals were precipitated prior to the addition of sulphide by pH adjustment alone. Iron (3+) and aluminium salts were difficult to dissolve. Based on these results (Table 4), selective precipitation of iron, nickel, and manganese is not possible as hydroxides.

Table 4. Precipitation as hydroxides of some metals by simple pH adjustment.

| Salt     | pH When Salt Dissolves | End pH | Precipitate Formed |
|----------|------------------------|--------|--------------------|
| NiSO$_4$ | 5                      | 8.8    | Yes                |
| Al$_2$(SO$_4$)$_3$ | 4.3 | 7.5    | No                 |
| FeSO$_4$ | 4.5                    | 6.0    | Yes                |
| MnSO$_4$ | 4.8                    | 7.5    | Yes                |
When the pH of the solution to be precipitated was raised to eight using NaOH, the metals began to precipitate as hydroxides. The NaOH precipitation was tested, and the results showed that not all may be precipitated as sulphides after raising the pH ≥ 8 before adding the HS\(^{-}\) solution (Table 5). An attempt was made to make a solution of several metals, but a precipitate was obtained in each of the three tests prior to the addition of hydroxide or sulphide. In a multi salt solution there are complex relationships with all ions going into an equilibrium which is determined by hydrolysis, complex formation, redox reactions and precipitations. During the precipitation of the mixtures, problems arose when dissolving all the compounds in the same solution. Some were already precipitated by adjusting the pH, and these were not always reproducible. Tin chloride was the most difficult to mix with others, and it completely precipitated the sample without any other additions (e.g., NaOH or HS\(^{-}\)), because it undergoes hydrolyses and forms Sn(OH)Cl which has a low solubility. Sn(II)-chloride is only stable in very acidic solutions and it is a strong reducing agent as well. [16] The only successful solution was to dissolve all metal salts separately. The pH of the solution to be precipitated cannot be raised too high because then the metals start to precipitate as hydroxides, as can be seen from Table 5.

| Metal | Weight [g] | Initial pH | Adjusted pH | Precipitate after Adjustment | Precipitate as Sulphide |
|-------|------------|------------|-------------|-----------------------------|-------------------------|
| Mg    | 0.0985     | 6.55       | 8.31        | Black/white                 |                         |
| Co    | 0.0754     | 8.47       |             | Black                       |                         |
| Cu    | 0.1907     | 5.03       | 8.11        | Blue                        | Green/brown             |
| Cd    | 0.0965     | 5.51       | 8.16        | White                       | Yellow                  |
| Zn    | 0.0730     | 7.34       | 8.04        | White                       | White                   |
| Sn    | 0.1112     | 2.55       | 8.14        | White/brown                 | Brown                   |
| Mn    | 0.0504     | 4.99       | 8.90        | Slowly dissolved            | Orange                  |
| Sb    | 0.1120     |            |             |                             |                         |
| Ce    | 0.1370     | 6.15       | 8.00        | Slowly dissolved            |                         |
| Al    | 0.0719     | 4.27       | 8.04        | Slowly dissolved            | White                   |
| Hg    | 0.1320     | 4.32       | 8.01        | Yellow                      | Black                   |
| Ni    | 0.0665     | 5.83       | 9.89        | White                       | Black                   |
| Sr    | 0.0802     | 7.40       | 8.38        | White                       |                         |
| Pb    | 0.1470     | 5.33       | 8.03        | White                       | Black                   |

1 ZnS is black as mineral due to the impurities, but the precipitated ZnS is pure and white, Manganese has several oxidation states, and MnS has typically red to brown colour.

The precipitation of multi-metal systems from the solution was performed at a pH of 8. In this way, soluble sulphide (HS\(^{-}\)) could be used for precipitation and to avoid the use of toxic gaseous hydrogen sulphide. The sulphide used for the precipitation was in the form of a completely gaseous \(\text{H}_2\text{S}\) at pH < 5. If HS\(^{-}\) is used for the precipitation under neutral conditions, pH > 7, the pH adjustment cost compared to lime precipitation could still be lower. Adjusting the pH to 5 or 6 is sufficient for precipitation as sulphides. For anaerobic treatment (i.e., biological sulphate reduction), the pH should be adjusted to a narrow pH range of about 7–8. The pH of the stock solution was above five after all metal salts had been dissolved. Some salts contained crystal water, which did not impair precipitation. The vessel was slowly stirred in a magnetic stirrer and settled. The precipitation endpoint was tested by adding the precipitation solution after 20 h, and no further reaction was achieved.
4.3. Two-Step Precipitation with First pH Adjustment Followed by Sulphide Precipitation Using Na₂S Solution

Another solution was made in the same way and the pH of the solution was 5–6, and no further adjustment was needed. Precipitation was performed with 2 g/L Na₂S solution adjusted to pH 8. Table 6 shows the values of metals precipitated with this Na₂S solution and with a starting solution of pH 5–6. The table shows precipitation at both higher and lower concentrations. The first precipitation was performed, and after this 10 mL of the solution was diluted to 1000 mL, and a second precipitation was performed. The results show that the initial concentration had little effect on the final result. The results in Table 6 are reproducible. However, there are exceptions. For example, lead with a sulphide Ks of $10^{-28}$ implies that the final concentration should be lower. The precipitation of tin was staggering. Its Ks is the same as that of lead. The values are close to each other when the magnitude is considered. Table 6 shows that the initial concentration does not affect the final precipitation. Sb and Ce did not precipitate as sulphides.

| Metal | Initial Concentration of First Precipitation [mg/L] | Final Concentration of First Precipitation [mg/L] | Initial Concentration of Second Precipitation [mg/L] | Final Concentration of Second Precipitation [mg/L] |
|-------|----------------------------------------------------|-------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| Cd    | 26.0                                               | $9.8 \times 10^{-3}$                            | 0.260                                            | $11.0 \times 10^{-3}$                            |
| Co    | 34.2                                               | $7.7 \times 10^{-3}$                            | 0.342                                            | $5.8 \times 10^{-3}$                             |
| Cu    | 76.0                                               | $2.4 \times 10^{-3}$                            | 0.760                                            | $<0.5 \times 10^{-3}$                            |
| Hg    | 48.8                                               | $0.6 \times 10^{-3}$                            | 0.488                                            | $6.2 \times 10^{-3}$                             |
| Mg    | 5.9                                                | $2.0 \times 10^{-3}$                            | 0.590                                            | $<0.13 \times 10^{-3}$                           |
| Mn    | 26.0                                               | $7.9 \times 10^{-3}$                            | 0.260                                            | $5.6 \times 10^{-3}$                             |
| Ni    | 15.2                                               | $20.1 \times 10^{-3}$                           | 0.152                                            | $9.7 \times 10^{-3}$                             |
| Pb    | 46.0                                               | $29.2 \times 10^{-3}$                           | 0.460                                            | $19.7 \times 10^{-3}$                            |
| Sn    | 34.8                                               | $<0.5 \times 10^{-3}$                           | 0.348                                            | $<0.5 \times 10^{-3}$                            |

Table 6 summarizes the results of two different precipitation experiments. All metals were precipitated separately. As the precipitating reagent solution is added, the volume of the solution to be precipitated changes and, at the same time, so does the concentration of the metals. Therefore, it is difficult to estimate the exact concentration of the metals prior to precipitation. Some metals were precipitated as hydroxide and some as sulphide and some as both according to XRD analysis. Figure 3 shows XRD spectra of precipitates from Pb, Mn, and Cu precipitation experiments.

The results of the precipitation experiment were compared to the Eh-pH plots (Figures S1–S15). As₂O₃ was not solubilized. Co should have been precipitated according to calculations, but at pH 8.47 it remained dissolved. Mg precipitates at pH 11.6, and thus it was not precipitated in the experiments. On the contrary, a white precipitate was obtained when sulphide was added. Strontium precipitates at pH 13.5 theoretically, but it was observed to precipitate at pH 9.9. Cu precipitated as indicated by the calculations. The theoretical pH value of Mn precipitation was pH 10.2, but the measured value was 8.9. The calculated value of Zn was pH 5.8, but the measured value was 8.04. The calculated value of Cd was pH 7 and it precipitated at 8.16. Sn and Hg precipitated as expected when compared to the calculations. Pb precipitated at pH 8.03, which is in line with the calculation. Al has three different forms above 5.8 and Ni precipitates theoretically at pH > 10, but the measured value was 8.38. It is also possible that Ni precipitates as NiSO₄·6H₂O. The calculation does not take this into account. Sb did not form any precipitate as indicated by the calculations. The sulphide precipitates, as shown in Table 4, were precipitated from the original solution, and no separate pH increase was required.
Sulphide precipitation is an efficient way to recover metals. Sulphide precipitation is also fast and inexpensive if it is produced in an anaerobic sulphate reduction. Biological sulphate reduction is not yet an established practice for the treatment of sulphate-containing wastewater, but it has a good chance of being used in a number of different sites. If the pH of the solution is lower than seven, the sulphide is partly in the hydrogen sulphide (H₂S) form. Evaporation of hydrogen sulphide from the solution can be dangerous if the volatile hydrogen sulphide content is very high. Hydrogen sulphide costs more than alkaline precipitants and reagent, but costs can be saved by first raising the pH with NaOH to above five, after which precipitation can be achieved using a solution of sulphide. The initial pH of the wastewater of mining is under four and it must be raised before precipitation, because this avoids the formation of gaseous H₂S. However, sulphide precipitation has also other benefits compared to hydroxide precipitation, such as the possibility of recovering other metals and much lower final metal concentrations. Hydroxide precipitates are considerably lighter than sulphide precipitates, and their settling is slow. It can be seen from Table 4 that most metals precipitate as hydroxides at pH 8 or over. Sulphide precipitation can be carried out with an HS⁻ solution adjusted to pH 8, and the pH of the solution to be precipitated can be adjusted to about 5.5. At very low pH, only a part of the metals can be precipitated because sulphide precipitates are acid soluble. However, as a result, theoretically it can be stated that the HS⁻ derived from biological sulphate reduction can be used for the precipitation of metals. However, the pH should not be too high, above eight, when metals begin to precipitate as hydroxides.

5. Conclusions

Na₂S is a highly efficient precipitant that achieves high removal of heavy metal cations from wastewater. Sulphide precipitation is an efficient way to recover metals. Sulphide precipitation is also fast and inexpensive if it is produced in an anaerobic sulphate reduction. Biological sulphate reduction is not yet an established practice for the treatment of sulphate-containing wastewater, but it has a good chance of being used in a number of different sites. If the pH of the solution is lower than seven, the sulphide is partly in the hydrogen sulphide (H₂S) form. Evaporation of hydrogen sulphide from the solution can be dangerous if the volatile hydrogen sulphide content is very high. Hydrogen sulphide costs more than alkaline precipitants and reagent, but costs can be saved by first raising the pH with NaOH to above five, after which precipitation can be achieved using a solution of sulphide. The initial pH of the wastewater of mining is under four and it must be raised before precipitation, because this avoids the formation of gaseous H₂S. However, sulphide precipitation has also other benefits compared to hydroxide precipitation, such as the possibility of recovering other metals and much lower final metal concentrations. Hydroxide precipitates are considerably lighter than sulphide precipitates, and their settling is slow. It can be seen from Table 4 that most metals precipitate as hydroxides at pH 8 or over. Sulphide precipitation can be carried out with an HS⁻ solution adjusted to pH 8, and the pH of the solution to be precipitated can be adjusted to about 5.5. At very low pH, only a part of the metals can be precipitated because sulphide precipitates are acid soluble. However, as a result, theoretically it can be stated that the HS⁻ derived from biological sulphate reduction can be used for the precipitation of metals. However, the pH should not be too high, above eight, when metals begin to precipitate as hydroxides.

Supplementary Materials: The following are available online at http://www.mdpi.com/2305-7084/4/3/51/s1. Figure S1: Eh-pH diagram of Co. Figure S2: Eh-pH diagram of Cu. Figure S3: Eh-pH diagram of Fe. Figure S4: Eh-pH diagram of Mg. Figure S5: Eh-pH diagram of Mn. Figure S6: Eh-pH diagram of Sr. Figure S7: Eh-pH diagram of Zn. Figure S8: Eh-pH diagram of Cd Figure S9: Eh-pH diagram of Sb. Figure S10: Eh-pH diagram of Ce. Figure S11: Eh-pH diagram of Hg. Figure S12: Eh-pH diagram of Sn. Figure S13: Eh-pH diagram of Pb. Figure S14: Eh-pH diagram of Al. Figure S15: Eh-pH diagram of Ni.

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