Jurnal Kejuruteraan 11 (2) 1999 85-101

# Removal of Mixed Heavy Metals by Hydroxide Precipitation

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## ABSTRACT

*Heavy metals such as chromium, nickel, copper, zinc and lead, can be effectively removed from metal finishing wastewaters by hydroxide precipitation. Prior to precipitation, ferrous sulphate is added to reduce chromium from hexavalent to trivalent state and also, to form stable complex ferrocyanides with cyanide. This batch study was carried out to evaluate the minimum pH range for the minimum solubility of metal hydroxide precipitation. All the metals (Cu, Ni, Zn, Pb and Cr) were present simultaneously in synthetic wastewaters. In the absence of cyanide, the maximum hydroxide precipitation for Cu, Ni, Zn, Pb and Cr occurred at pH ranges of 6.5-12, 9-12, 8.5-12, 8.5-12 and 8-12 respectively. When cyanide was added into the wastewater, only pH range of minimum solubility for Cu was shifted to pH 8.5-12. For other metals, their pH ranges were not affected by the presence of cyanide. In addition, stable complex ferrocyanides precipitated optimally starting at pH 9.*

## ABSTRAK

*Logam berat seperti kromium, nikel, kuprum, zink dan plumbum, dari air sisa penyudahan logam boleh disingkirkan melalui pemendakan hidroksida. Sebelum proses pemendakan dijalankan, larutan ferus sulfat terlebih dahulu ditambahkan untuk menurunkan kromium heksavalen kepada bentuk trivalennya, dan juga untuk membentuk mendakan stabil kompleks ferosianida dengan sianida. Kajian ini telah dijalankan untuk mendapatkan satu julat pH optimum bagi memendakkan kesemua logam hidroksida yang terlibat. Kesemua logam (Cu, Ni, Zn, Pb, dan Cr) tersebut hadir dalam bentuk campuran dalam air sisa sintetik. Pemendakan hidroksida yang maksimum, tanpa kehadiran sianida, untuk logam Cu, Ni, Zn, Pb, Cr didapati berlaku masing-masing pada julat pH 6.5-12, 9-12, 8.5-12, 8.5-12 dan 8-12. Apabila sianida wujud dalam air sisa, hanya julat pH untuk kebolehlarutan minimum Cu teranjak kepada pH 8.5-12. Untuk logam-logam lain, kehadiran sianida tidak memberi kesan ke atas julat pH bagi kebolehlarutan minimum mereka. Manakala, kempleks stabil ferosianida mula mendak dengan optimumnya bermula dari pH 9.*

## INTRODUCTION

Heavy metals from metal finishing waste, notably electroplating waste, such as cadmium, chromium, copper, nickel, zinc as well as cyanide, are highly toxic and can cause irreversible damage to the environment. As restrictions on effluent discharges are tightened, the control of these discharges becomes more important. Conventional methods of heavy metal treatment in general perform satisfactorily to meet direct discharge requirements. Hydroxide precipitation is the most common method on the basis of its performance, ease of operation and cost (Tünay & Kabdasli 1993; Christensen & Delwiche 1982).

The solubilities of most electroplating metals are function of pH value. The optimum pH value for better precipitation may be different for each metal ion. Metals precipitate at various pH levels depending on such factors as the metal itself, the insoluble salt that has been formed (for example, hydroxide, carbonate, sulphide) and the presence of complexing agents such as ammonia, EDTA, cyanide and citric acid. It is apparent that when two or more heavy metals are found in the same stream, the optimum pH for precipitation may be different for each ion. In addition to these heavy metals, a number of complexing agents may be present that could severely influence the precipitation efficiency (Lanouette 1977).

This research investigated some aspects of the feasibility of applying hydroxide precipitation as a treatment method for mixed-metal finishing wastewater, such as those from electroplating industries. The specific goal has been to examine the solubility behaviour of Cu, Ni, Zn, Pb and Cr in the absence and presence of complexing agent, $CN^-$, in order to locate one pH or a pH range which will produce satisfactorily, though not optimum, hydroxide insolubility for each of the metal ions present in the wastewater, in order to precipitate them simultaneously.

Previous works with hydroxide precipitation (Christensen & Delwiche 1982; Patterson 1985; Tünay & Kabdasli 1994) have mostly been performed in well-controlled systems containing only one or two metals. In this work, mixed synthetic systems containing five different cations (Cu, Ni, Zn, Pb and Cr(VI)) were used. In addition, the effect of complexing agent, $CN^-$ on hydroxide precipitation was also evaluated.

## THEORETICAL CONSIDERATIONS

The solubility of metal hydroxide is defined by solubility product ($K_s$) and by equations relating the metal hydroxide solid species in equilibrium with soluble metal hydroxide species (Patterson 1982; Stumm & Morgan 1981). The following equilibrium equations may be used to describe the solubility curve of a divalent metal hydroxide, $M^{2+}$:

$$M(OH)_2(s) \rightleftharpoons M^{2+} + 2OH^- \qquad K_{s0} \qquad (1)$$

$$M(OH)_2(s) \rightleftharpoons M(OH)^+ + OH^- \qquad K_{s1} \qquad (2)$$

$$M(OH)_2(s) \rightleftharpoons M(OH)_2^0 \qquad K_{s2} \qquad (3)$$

$$M(OH)_2(s) + OH^- \rightleftharpoons M(OH)_3^- \qquad K_{s3} \tag{4}$$

$$M(OH)_2(s) + 2OH^- \rightleftharpoons M(OH)_4^{2-} \qquad K_{s4} \tag{5}$$

Each of these equations describes an equilibrium reaction between solid phase, $M(OH)_2(s)$, and a soluble species of the metal, M. According to the definition of solubility product, all the above equations can be rewritten as follows :

$$K_{s0} = [M^{2+}][OH^-]^2 \tag{6}$$

$$K_{s1} = [M(OH)^+][OH^-] \tag{7}$$

$$K_{s2} = [\,M(OH)_2^0\,] \tag{8}$$

$$K_{s3} = \frac{[M(OH)_3^-]}{[OH^-]} \tag{9}$$

$$K_{s4} = \frac{[M(OH)_4^{2-}]}{[OH^-]^2} \tag{10}$$

Using the logarithmic form, substituting $\{\log[OH^-]=pH-14\}$ (based on the self-ionization of water) and rearranging, the following equations are obtained :

$$\log[M^{2+}] = \log K_{s0} - 2pH + 28 \tag{11}$$

$$\log[M(OH)^+] = \log K_{s1} - pH + 14 \tag{12}$$

$$\log[M(OH)_2^0] = \log K_{s2} \tag{13}$$

$$\log[M(OH)_3^-] = \log K_{s3} + pH - 14 \tag{14}$$

$$\log[M(OH)_4^{2-}] = \log K_{s4} + 2pH - 28 \tag{15}$$

Equations (11)-(15) give the total soluble species of hydroxide solubility for a divalent metal which exist at equilibrium. Table 1 summarises all the equilibrium reactions of soluble species for metals, including the trivalent metal, $Cr^{3+}$, all of which will be studied in this work. Each of the equations involved may be plotted for any metal, using the appropriate solubility constants, to define the metal solubility curve.

Figure 1 represents theoretical curves of metal hydroxide solubility for Cu(II), Zn(II), Ni(II), Pb(II) and Cr(III) which were plotted using equilibrium constants listed in Table 1. For each solubility curve in Figure 1, there is a value or a range of pH where hydroxide solubility is at minimum level for each metal ion. These values of optimum pH associated with that minimum solubility are listed in Table 1. In the more acidic and alkaline region, that is outside of the optimum pH range, the solubility of metal hydroxide increases. As a summary, a metal solubility can be divided into three main parts : stabilization, destabilization and

TABLE 1. Equlibrium reactions with their respective equalibrium constant, involved in hydroxide solubility

| Metal | Equilibrium reactions | Log Equilibrium Constants, $K_{s0}$, $K_{s1}$, $K_{s2}$, $K_{s3}$, $K_{s4}$ at 25°C, I=0 | pH of minimum solubility | Reference |
|---|---|---|---|---|
| $Cu^{2+}$ | $Cu(OH)_2(s) = Cu^{2+} + 2OH^-$ | -19.08 | 7.5-11.5 | Stumm & Morgan (1981); Patterson (1982) |
| | $Cu(OH)_2(s) = Cu(OH)^+ + OH^-$ | -13.08 | | |
| | $Cu(OH)_2(s) = Cu(OH)_2^0$ | -6.28 | | |
| | $Cu(OH)_2(s) + OH^- = Cu(OH)_3^-$ | -3.88 | | |
| | $Cu(OH)_2(s) + 2OH^- = Cu(OH)_4^{2-}$ | -2.98 | | |
| $Zn^{2+}$ | $Zn(OH)_2(s) = Zn^{2+} + 2OH^-$ | -16.0 | 8.9-10.3 | Patterson (1982); Christensen & Delwiche (1982); Tünay *et al.* (1992) |
| | $Zn(OH)_2(s) = Zn(OH)^+ + OH^-$ | -11.9 | | |
| | $Zn(OH)_2(s) = Zn(OH)_2^0$ | -5.9 | | |
| | $Zn(OH)_2(s) + OH^- = Zn(OH)_3^-$ | -1.8 | | |
| | $Zn(OH)_2(s) + 2OH^- = Zn(OH)_4^{2-}$ | -0.5 | | |

*continued*

TABLE I continued

| Metal | Equilibrium reactions | Log Equilibrium Constants, $K_{s0}$, $K_{s1}$, $K_{s2}$, $K_{s3}$, $K_{s4}$ at 25°C, I=0 | pH of minimum solubility | Reference |
|---|---|---|---|---|
| $Ni^{2+}$ | $Ni(OH)_2(s) = Ni^{2+} + 2OH^-$ | -14.7 | 9.3-10.5 | Christensen & Delwiche (1982) |
| | $Ni(OH)_2(s) = Ni(OH)^+ + OH^-$ | -10.9 | | |
| | $Ni(OH)_2(s) = Ni(OH)_2^0$ | -3.9 | | |
| | $Ni(OH)_2(s) + OH^- = Ni(OH)_3^-$ | -1.7 | | |
| $Pb^{2+}$ | $Pb(OH)_2(s) = Pb^{2+} + 2OH^-$ | -14.9 | 10.0 | Patterson (1982); Benefield et al. (1982); Wallace & Singer (1981) |
| | $Pb(OH)_2(s) = Pb(OH)^+ + OH^-$ | -9.1 | | |
| | $Pb(OH)_2(s) = Pb(OH)_2^0$ | -4.1 | | |
| | $Pb(OH)_2(s) + OH^- = Pb(OH)_3^-$ | -1.0 | | |
| $Cr^{3+}$ | $Cr(OH)_3(s) = Cr^{3+} + 3OH^-$ | -30.0 | 8.2 | Christensen & Delwiche (1982) |
| | $Cr(OH)_3(s) + 2H^+ = Cr(OH)^{2+} + 2H_2O$ | 8.0 | | |
| | $Cr(OH)^{2+} + H_2O = Cr(OH)_2^+ + H^+$ | -6.2 | | |
| | $Cr(OH)_3(s) + OH^- = Cr(OH)_4^-$ | -0.4 | | |
| | $2Cr^{3+} + 2H_2O = Cr_2(OH)_2^{4+} + 2H^+$ | -4.0 | | |

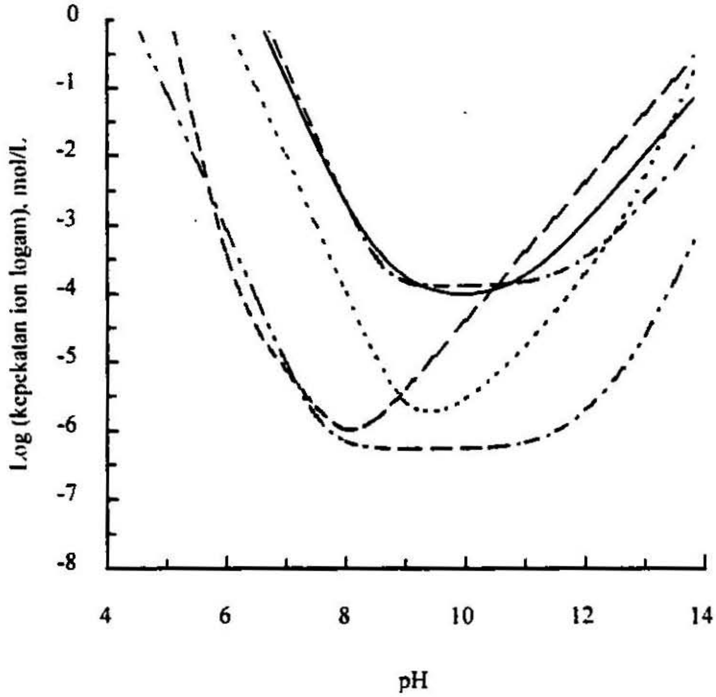


FIGURE 1. Concentration of soluble metal ion hydroxide products in equilibrium with their respective insoluble hydroxides as a function of pH

*Note:* – — *Cu(II)* — *Zn(II)* — - — - *Ni(II)* ——— *Pb(II)* — — — *Cr(III)*

restabilization. Below the optimum pH of minimum solubility, stabilized colloid of positive charge exists, whereas negatively-charged colloid exists in the region of restabilization above the optimum pH. In the intermediate region that is within the optimum pH, destabilization of colloid occur where metal hydroxides flocculate and forms precipitates optimally (Thomas & Theis 1976).

Generally, the actual solubility of a metal hydroxide deviates from the theory. The deviations may occur due to lack of equilibrium conditions, ionic strength effects, inability to analytically differentiate between true soluble and colloidal substances, and the presence of complexing agents (Patterson 1982). This study will look through any deviation that might occur in the actual solubility curve compared to the theoretical curve.

## MATERIALS AND METHODS

### SYNTHETIC WASTEWATERS

Reagent grade chemicals (Merck, Germany) were diluted with distilled water in all test solutions. Batch hydroxide precipitation experiments with synthetic wastes were conducted using sulphate salts for all cations (Cu, Ni, Zn, Pb)except for Cr(VI), where $K_2Cr_2O_7$ was used, and potassium salt for anion (KCN).

The synthetic wastes were made in the form of stock solutions in order to maintain the metal ion concentrations and also for safety reasons. Five different stock solutions of synthetic wastes were prepared, each containing all the five metal ions simultaneously at different concentrations and each stock represented one dominant cation. The concentrations of all metals in each stock solution were chosen at random, based on the report for the Department of Environment, Malaysia (Rakmi et al., 1991). These stock solutions were diluted for experimental needs. All the initial concentrations of the five metal ions and cyanides in the solutions were listed in respective figures of Fig. 1a-e and Fig. 2a-f (in legends). 0.5 L of 55.6 g/L $FeSO_4.7H_2O$ solution, as a reducing agent to the hexavalent chromium, was freshly prepared in each experimental run since it is easily oxidised to its trivalent state. 18.5 g/L $Ca(OH)_2$ was used for pH adjustment and also for metal precipitation.

## BATCH HYDROXIDE PRECIPITATION TESTS

Four L of synthetic waste was prepared in a 5 L beaker for each experiment run. The experiments were performed in an open system with rapid stirring by a mechanical mixer (Voss of Moldon, Essex) at 100 rpm. Ferrous sulphate, $FeSO_4.7H_2O$ was added in excess to ensure complete reduction of Cr from hexavalent to its trivalent state, as well as to induce cyanide complexation to form stable complex of ferrocyanide precipitates, for the case where cyanide was added to the synthetic waste. The reduced chromium and other heavy metals are then precipitated as hydroxides. Following reduction, the pH was readjusted by a unit increment in each step with $Ca(OH)_2$ until a pH value of 12-13. For each pH increment, the reaction was allowed to take place for 30 minutes and then, a 30 mL aliquot of suspension was collected for metal and cyanide analysis.

## ANALYTICAL METHODS

Whatman membrane filters of 0.45 µm pore size, with the aid of Millipore vacuum pump (Millipore Corporation, Bedford), were used to filter the aliquots of samples collected at each selected pH. After being filtered, the filtrates were acidified with a 65% nitric acid for preservation until the pH reached less than pH 2 and stored for metal analysis. However, the analysis of cyanides was carried out immediately after samples being collected and filtered, and before the filtrates being acidified because the addition of acid could reduce the actual content of cyanides in the sample. The concentrations of Cr(VI) and free cyanides were respectively determined colorimetrically according to *1,5 Diphenylcarbohydrazide* method at 540 nm and *Pyridine-Pyrazalone* method at 612 nm. Both the determinations of Cr(VI) and $CN^-$ were analyzed by means of a Hach DR/2000 Spectrophotometer Model 44800-00 (Colo, U.S). All metals were detected using direct flame atomic absorption spectrophotometry (Perkin-Elmer Model 1100B). All determinations were according to Standard Methods (APHA 1992).

The pH was measured in the suspensions to within 0.01 unit with a Schott combination glass-reference electrode and Schott pH Analyzer Model 672P (Great Lakes Instrument, US). The electrode was calibrated with a two point calibration using pH buffer solutions of pH 4 and 7 equilibrated to the preset temperature. pH calibration was checked periodically and adjusted if necessary.

## RESULTS AND DISCUSSION

### HYDROXIDE PRECIPITATION IN SYNTHETIC NON-COMPLEXING SYSTEMS

The results of hydroxide precipitation with only metals present (i.e. no complexing agents) are presented in Figures 2a-e (All y-axes in the figures were drawn on logarithmic scale). The figures show that each metal has its minimum solubility at different pH range. The optimum insolubilities of hydroxide precipitation for Cu, Ni, Zn, Pb and Cr occurred at pH ranges of 6.5-12, 9-12, 8.5-12, 8.5-12 and 8-12 respectively, regardless the initial metal concentration in each experimental run. It can be concluded that simultaneous precipitation of all the existing metal ions (Pb$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$) in the wastewater can be carried out optimally at pH range as minimum as pH 8.5-9.

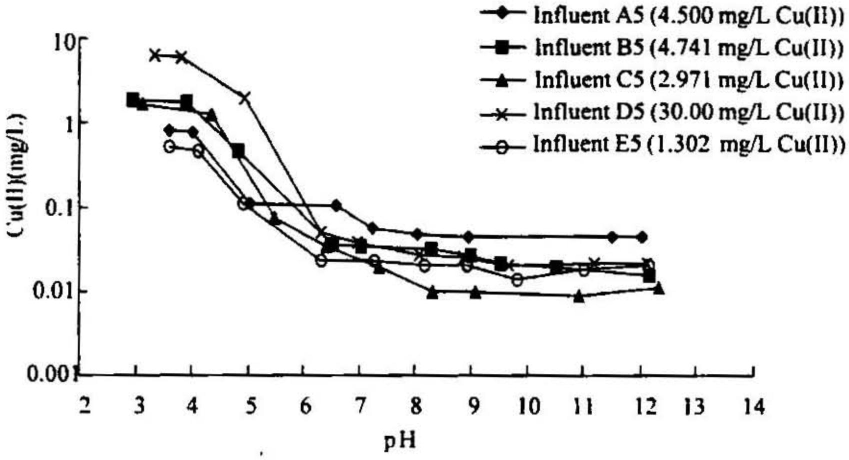


FIGURE 2a. Precipitation of Cu as hydroxides in non-complexing systems of mixed-metal wastes

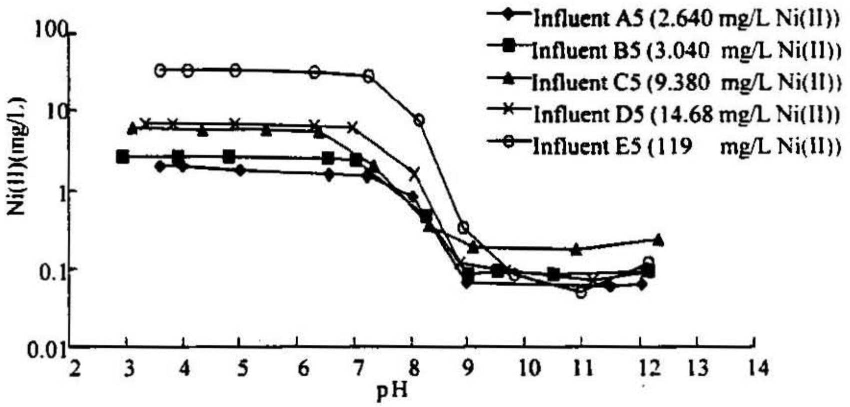


FIGURE 2b. Precipitation of Ni as hydroxides in non-complexing systems of mixed-metal wastes

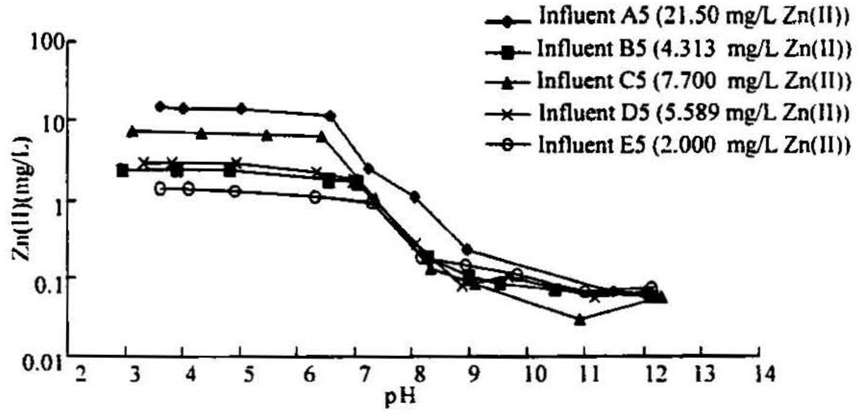


FIGURE 2c. Precipitation of Zn as hydroxides in non-complexing systems of mixed-metal wastes

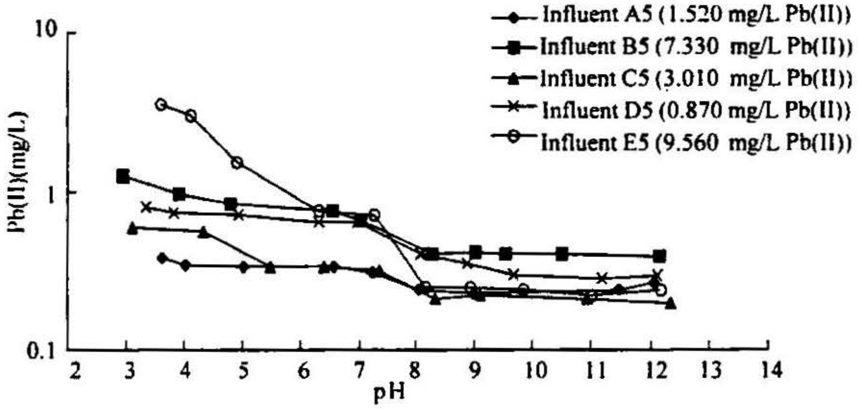


FIGURE 2d. Precipitation of Pb as hydroxides in non-complexing systems of mixed-metal wastes

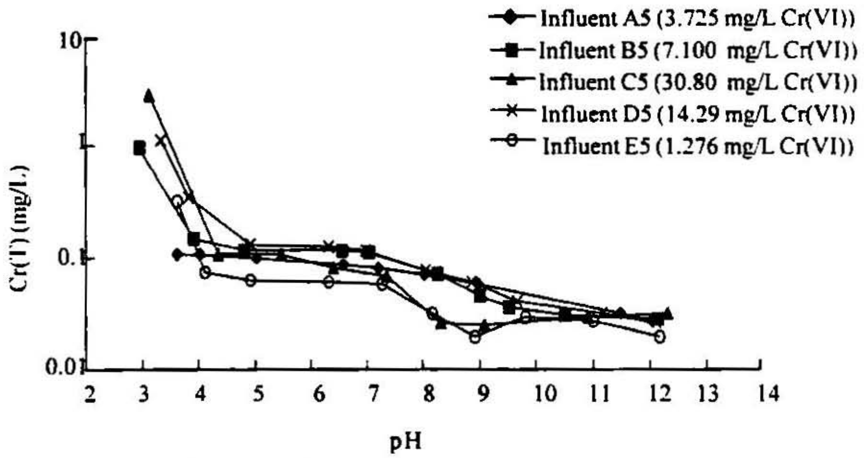


FIGURE 2e. Precipitation of Cr as hydroxides in non-complexing systems of mixed-metal wastes

Table 2 compares the pH values of optimum solubility for hydroxide precipitation of mixed-metal ions with others' work. According to the results of this study as shown in Table 2, there is a slight difference in the optimum pH chosen to simultaneously precipitate all the existing metal ions. This might due to the different kinds of precipitating agent used to precipitate metals, and different reducing agent used to reduce chromium hexavalent and metal ions existing in mixed-metal wastewater. The presence of anions in high concentrations, such as sulphate and carbonate, and also absorption of $CO_2$ from atmosphere during mixing can also affect the hydroxide precipitation (Patterson et al. 1976; Thomas & Theis 1976).

All the solubility curves of the metal hydroxide precipitation (Figures 2a-e) show stabilization characteristics in low pH ranges and no restabilization occurs at high pH after going through their minimum solubility stage. These findings agree with those obtained by Nilsson (1971) and Thomas and Theis (1976) in their research. There are two explanations for this phenomenon. First, $Ca^{2+}$ ion from lime slurry which was used as the precipitating agent and also for pH increment, has acted as a doubly charged counter-ion to the negatively charged colloid present at high pH. As a result, the stabilized negatively charged colloid will be destabilized by $Ca^{2+}$ ions and this allows coagulation of the hydroxide precipitate continues to occur at higher pH. Moreover, according to Schulze-Hardy rule, $Ca^{2+}$ ions are capable to destabilize a negatively charged colloid 100 times stronger than $Na^{+}$ ions (O'Melia 1972).

Secondly, the co-precipitation role of ferric hydroxide during hydroxide precipitation can also be taken into account to explain why no restabilization occurs at high pH. In the reduction process of $Cr^{6+}$ by ferrous sulphate, $Fe^{2+}$ ions were oxidised to $Fe^{3+}$ ions. The formed $Fe^{3+}$ ions would precipitate as ferric hydroxide, $Fe(OH)_3$ at high pH and co-precipitate with other metal ions (Benefield et al. 1982; Brooks 1991; Clifford et al. 1986; Schwitzgebel 1992; Stumm & Morgan 1981; Thomas & Theis 1976). The mechanism responsible in this case is the enmeshment action of the large volume of ferric hydroxide floc formed. As this floc formed, other colloidal particles of other metals become enmeshed and

TABLE 2. Comparison of optimum pH range for minimum solubility of mixed-metal ions with other studies

| Reference | Metal ions (Optimum pH for individual metal) | | | | | | | | Optimum pH | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| | Pb | Cr | Cu | Ni | Zn | Cd | Fe | Ag | | |
| This study (1998) | ✓ (8.5-12) | ✓ (8-12) | ✓ (6.5-12) | ✓ (8.5-12) | ✓ (7.5-12) | - | - | - | 8.5-9.0 | $Cr^{6+}$ was reduced by $FeSO_4.7H_2O$ in acidic medium; $Ca(OH)_2$ was used as precipitating agent; $SO_4^{2-}$ was the dominant anion |
| Schwitzgebel (1992) | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | - | ✓ | 9.5 | $CN^-$ was removed through oxidation by hipochlorite; Reduction of $Cr^{6+}$ by $FeSO_4.7H_20$ and metal precipitation were proceeded simultaneously at pH 9.5; NaOH was used as the precipitating agent |
| Patterson *et al.* (1976) | ✓ (10.5) | - | - | ✓ (11.0) | ✓ (9.5) | ✓ (10.4) | - | - | - | NaOH was used as the precipitating agent; $10^{-3.6}$ mol/L total carbonate exist. |
| Thomas & Theis (1976) | - | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | - | - | $Cr^{6+}$ was reduced by $FeSO_4.7H_2O$ at pH 4; Optimum precipitation of $Cr(OH)_3$ achieved respectively at pH 6.5-8.5 and 6.5-11.5 when NaOH and $Ca(OH)_2$ were used. |
| Sheffield (1982) | ✓ | - | ✓ | ✓ | - | - | - | - | 8.5 | $Ca(OH)_2$ was used as the precipitating agent; $Na_2S$ added to enhance $Pb^{2+}$ insolubility. |
| Kreye *et al.* (1979) | - | ✓ | - | - | ✓ | - | ✓ | - | 9.5 | NaOH was used as the precipitating agent; $Cr^{6+}$ was reduced by $Na_2S_2O_5$ at pH 2-3. |
| Scott (1978) | - | ✓ | ✓ | ✓ | ✓ | ✓ | - | - | 9.0 | $Ca(OH)_2$ was used as the precipitating agent; no complexing agent present. |

swept from the system as it settles (Benefield et al. 1982; Thomas & Theis 1976).

Since no restabilization occurs at high pH, controlling pH during hydroxide precipitation process by using lime will became easier and not be critical. No acid addition is required to decrease the pH to the set point level since the solubility of metals still remain at minimum although the suspension pH has overshoot the optimum pH where the optimum solubility of metals occurs.

## HYDROXIDE PRECIPITATION IN THE PRESENCE OF CYANIDE

The results of each metal solubility in the presence of cyanide as a complex former were shown in Figures 3a-f (All y-axes were drawn in logarithmic scale). and were summarised in Table 3. The table compares the optimum pH for each metal in hydroxide precipitation in non-complexing systems with those in the presence of cyanide. Cyanide forms strong complexes with several heavy metals such as Fe, Zn, Cu and Ni (Sharpe 1976). When cyanide was added into the wastewater, only pH range of maximum insolubility for Cu was shifted to pH 8.5-12 (Figure 3a). The effect on Cu, on the other hand, is somewhat unexpected. since Cu(II) is not complexed at all by cyanide. However, Cu(II) can be reduced to Cu(I) by CN. and Cu(I) forms strong complexes with $CN^-$ (Griffith. 1962: Stiff. 1971). The addition of cyanide has also caused a lag period to the Cu solubility curves due to the complexation of Cu(I) (Fig. 3a compared with Fig. 2a). For other metals, their pH ranges were not affected by the presence of cyanide (Figures 3b-e). The solubility curves of Pb and Cr are not dramatically different compared to those of CN-free systems. Nickel is the one most strongly complexed by $CN^-$ (Kunz et al. 1978), but there is no significant changes to the pH range and also to the trend of the Ni solubility curves when cyanide was added, compared with those of the non-complexing system. For Zn, the affinity of ferrous ions for cyanide will result in the zinc-cyanide complex to be broken according to the following reaction :

$$3Zn(CN)_4^{2-} + 2Fe^{2+} \rightleftharpoons 3Zn^{2+} + 2Fe(CN)_6^{4-} \qquad (16)$$

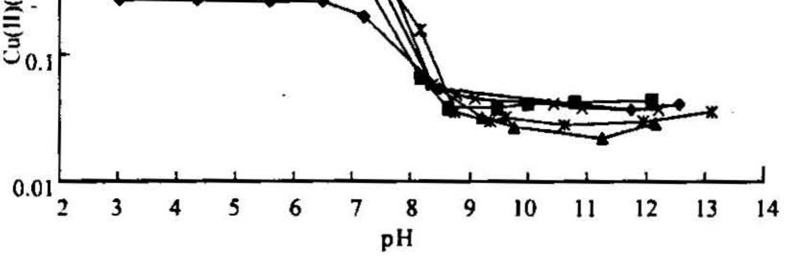


FIGURE 3a. Precipitation of Cu as hydroxides in the presence of cyanide in mixed-metal wastes

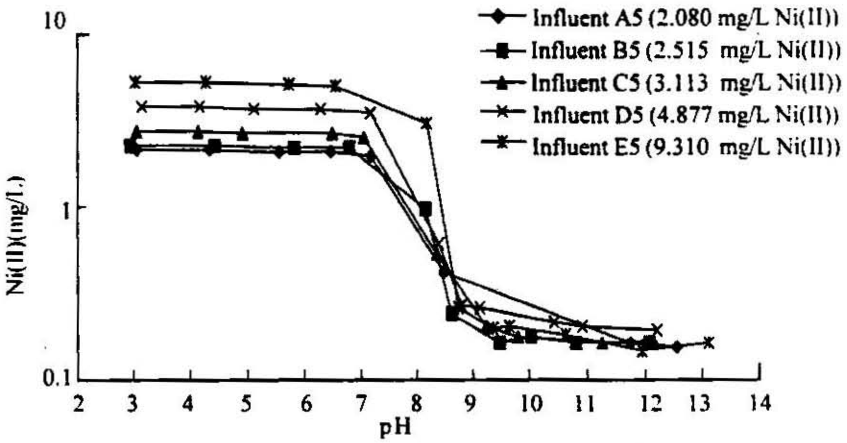


FIGURE 3b. Precipitation of Ni as hydroxides in the presence of cyanide in mixed-metal wastes

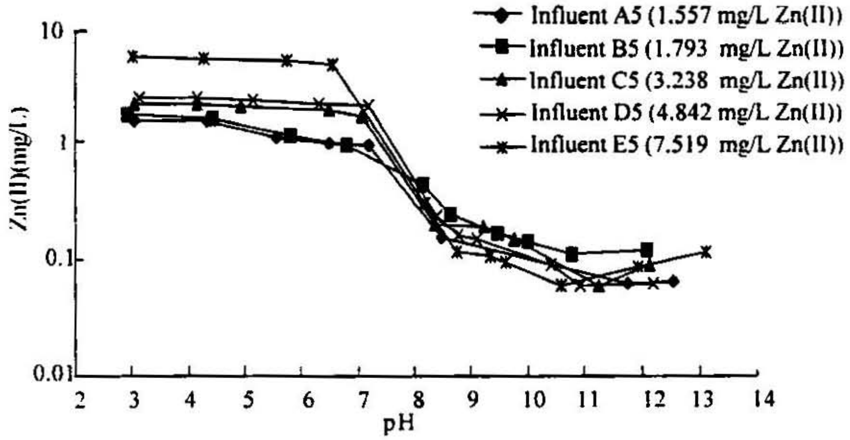


FIGURE 3c. Precipitation of Zn as hydroxides in the presence of cyanide in mixed-metal wastes

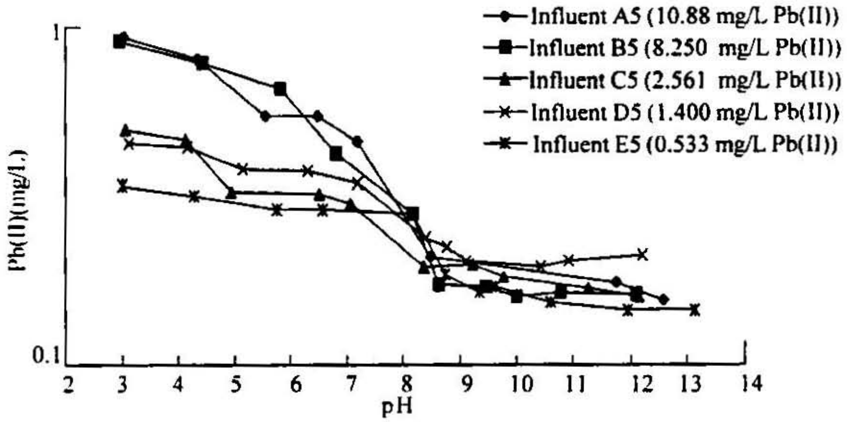
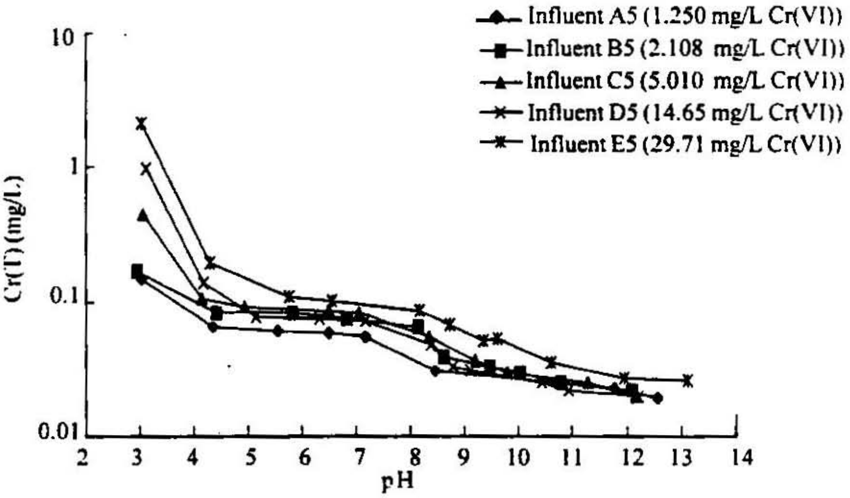


FIGURE 3d. Precipitition of Pb as hydroxides in the presence of cyanide in mixed-metal wastes



FIGUER 3e. Precipitation of Cr as hydroxides in the presence of cyanide in mixed-metal wastes

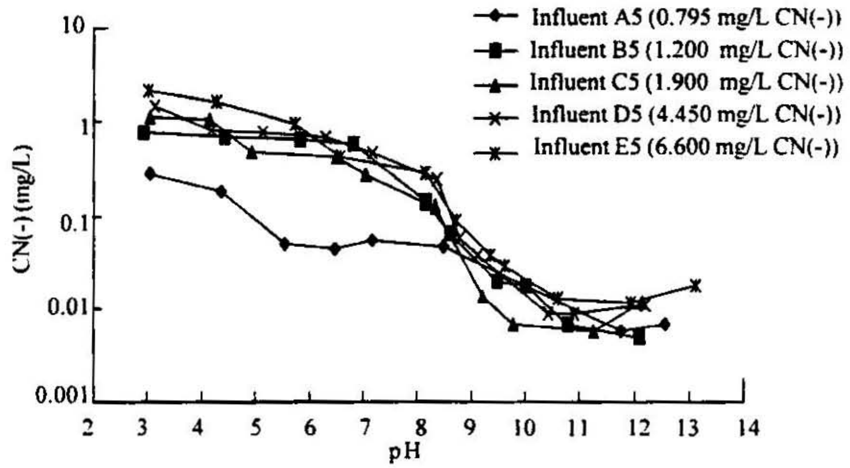


FIGURE 3f. Precipitation behaviour of CN as complex ferrocyanides in mixed-metal wastes

TABLE 3. Comparison of optimum pH for hydroxide precipitation in non-complexing system with those in the presence of cyanide

| Metal (including cyanides) | Optimum pH | |
|---|---|---|
| | Without complexing agents | With cyanide presence |
| Pb | 8.5-12 | 8.5-12 |
| Cr | 8-12 | 8-12 |
| Cu | 6.5-12 | 8.5-12 |
| Ni | 9-12 | 9-12 |
| Zn | 8.5-12 | 8.5-12 |
| CN | - | 9-12 |

Thus, zinc-cyanide complex is converted to free zinc ion, which will be precipitated as zinc hydroxide plus soluble ferrocyanide, which will be precipitated as prussian blue in the present of excess ferrous ion (Rice & Herman 1986), as follows :

$$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2 \downarrow \qquad (17)$$

$$Fe(CN)_6^{4-} + 2Fe^{2+} \rightleftharpoons Fe_2Fe(CN)_6 \downarrow \qquad (18)$$

These reactions explain why no abrupt changes of Zn solubility curves in cyanide systems are observed in this study. In addition, minimum residual cyanide is achieved by pH 9 (Figure 3f) when cyanide combined with ferrous ions to form stabilised ferrocyanide precipitates.

The results obtained in this study will be used in further runs to obtain correlations between pH and concentration effects of each metal with a change in lime dosages. These correlations will enable a rule base for optimum treatment process to be formulated. An intelligent automated controller based on fuzzy logic will be suitable for controlling this process which cannot be precisely described using a mathematical model. The fuzzy logic controller will monitor the status of the process on-line and determine the optimum dosage of precipitating agent (lime) required based on the derived rule base.

## CONCLUSIONS

From the foregoing discussions, it can be concluded that pH as minimum as 8.5 can be selected as the optimum pH for treating mixed-metal finishing wastes (Cu, Ni, Zn, Cr and Pb) by hydroxide precipitation in free-cyanide systems and pH 9 for the case in the presence of cyanide. At pH greater than 8.5-9, no restabilization of colloid are observed for all the metals involved. Consequently, controlling pH during hydroxide precipitation at the optimum pH will be easier and not too critical. Further studies will be carried out to obtain more correlations on variables such as turbidity of effluent and metal concentrations versus variations in flocculant and reducing agent dosages. These correlations form important parameters, which will be used in setting up fuzzy logic control of the whole process.

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