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THE RECOVERY OF Fe, Mn AND Al FROM A MINE WATER EFFLUENT

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Abstract—The mine water effluent investigated contains considerable quantities of Fe. Mn and Al. Recovery of the pure metals is obstructed by the presence of impurities such as Zn, Ni, Co, Cu and Th. The oxidation of the effluent results in practically complete separation of Fe and Mn, though both fractions contain Al as an impurity. A variety of important experimental results are discussed.

INTRODUCTION

Large quantities of dissolved metals are present in the effluents of various South African gold mines. The mine effluent concerned in this investigation is strongly acidic and contains approximately $3\,g\,l^{-1}$ Mn, $2{\cdot}2\,g\,l^{-1}$ Fe and $2{\cdot}5\,g\,l^{-1}$ Al, as well as trace quantities of Zn, Ni, Co, Cu and Th. At a flow rate of approximately $6800\,l.\,min^{-1}$ the recovery of these metals could be of economic significance especially if recovery of these metals from all gold mines could be achieved. Presently the acid contents of the effluent which is practically discharged every day, requires neutralization with lime before it can be discharged. This suggests a neutralization process to precipitate and separate the metals present as at least part of a recovery scheme.

Manolitsis, Matic and Mrost (1964) succeeded in recovering Ni and Co from a South African uranium extraction plant effluent on laboratory scale. Figure 1 shows their results for the precipitation of Fe, Mn and Al using synthetic test solutions. These results suggest the possibility of precipitating Fe and Al at $pH \leqslant 5$ while Mn remains in solution. Experiments performed on actual mine effluent showed that Mn co-precipitates at $pH \geqslant 3{\cdot}0$ thus obstructing a pure separation of the metals.

In this paper we report some preliminary results in an attempt to devise methods for the removal of Fe, Mn and Al. The possibilities studied include oxidation, precipitation, complexation and separation by the formation of aluminates at high pH.

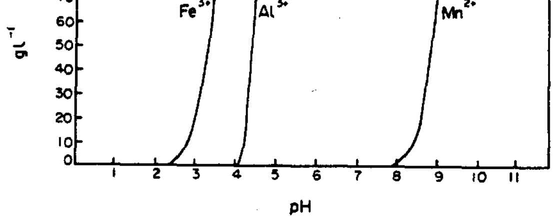


Fig. 1. pH-dependence of the precipitation of Fe, Mn and Al according to Manolitsis (1964).

EXPERIMENTAL

The effluent samples were obtained from a mine in the vicinity of Klerksdorp. The samples were stocked in dark stoppered 5-l. flasks after treatment with nitrogen to remove the oxygen present. This treatment allowed the samples to be stocked for long periods without any noticeable changes in concentration.

The ions Fe^{2+} and Fe^{3+} were analysed by means of standard laboratory procedures (Vogel, 1968), Al^{3+} was titrated with $ZnCl_2$ after complexation with Tritriplex III, using dithizon as indicator (Merck, 1970) and Mn^{2+} was determined colorimetric by oxidising the ion with KBr in 8 M H_2SO_4, the absorbance measurements being made at 500 nm ($\epsilon = 3510$). None of these methods of analysis when performed for the determination of one particular ion are affected by the presence of the other metal ions. The accuracy of the various analytical measurements lies within the following ranges: $Mn^{2+} \pm 6\%$, $Al^{3+} \pm 0{\cdot}05\,g\,l^{-1}$, $Fe^{2+} \pm 0{\cdot}05\,g\,l^{-1}$, $Fe^{3+} \pm 0{\cdot}08\,g\,l^{-1}$.

Measurements of pH were performed on a Metrohm E 300 B pH meter and absorbance measurements on a Carl-Zeiss spectrophotometer. The ozone used in this investigation was obtained from three reaction tubes to which a high voltage power supply (7000 V) was connected. Ozone concentrations were determined by treating samples with KI, followed by standard iodine titration with $Na_2S_2O_3$ (1 ml 0·1 N $Na_2S_2O_3 \equiv 2{\cdot}4$ mg O_3). During the treatment of the effluent with ozone, a vibro-mixer was used to improve the contact between the water and the ozone bubbles. Chemicals of analytical grade were used throughout the investigation.

The variation in quality of the effluent can be seen from the following analytical data of three different samples collected during a period of 1 yr.

$g\,l^{-1}$	Sample 1	Sample 2	Sample 3
Mn^{2+}	3·10	2·91	2·87
Fe^{2+}	0·75	0·89	0·53
Fe^{3+}	1·46	1·24	1·56
Al^{3+}	2·60	2·65	2·54

RESULTS AND DISCUSSION

The precipitation of Mn^{2+}, Al^{3+}, Fe^{3+} and Fe^{2+} present in the acidic effluent was studied as function of pH. The concentration of the metal ions that remain in solution, is plotted as a function of pH in Fig. 2. The obtained curves are not exactly in agreement with those of Manolitsis shown in Fig. 1. The differences are probably due to Manolitsis's use of ideal synthetic mixtures compared to the real mine effluent concerned in this investigation. It is seen from Fig. 2 that Mn^{2+} and Al^{3+} precipitate over a wide pH range, thus preventing the separation of the metal ions by means of a neutralisation–precipitation procedure. It is evident from Fig. 3 that the curve of Mn^{2+} is improved and the precipitation correspondingly confined to a smaller, more definite pH range by oxidising the test samples. The concentration of Fe^{3+} is considerably increased by the oxidation of Fe^{2+} to Fe^{3+}. The oxidation was accomplished with the following.

1. *Oxygen*

The reaction follows second order kinetics (Water Pollution Control Research, 1970) with the disadvantage that the oxidation rate decreases with decreasing oxygen concentration. This was eliminated by using a large excess of oxygen by which the oxidation kinetics is changed to pseudo first-order.

2. *Hydrogen peroxide*

The oxidation process, which is more effective than oxidation by oxygen and instantaneous on good stirring, proceeds according to the reactions

$$H_2O_2 \rightleftharpoons H_2O + O$$
$$4Fe^{2+} + 2O \rightarrow 4\,Fe^{3+} + 2O^{2-}.$$

It follows that 0·85 cm^3 of a 30% hydrogen peroxide solution is required to oxidise 1 litre of the mine effluent. Experimentally 1·2 $cm^3\,l^{-1}$ of effluent was added to ensure complete oxidation.

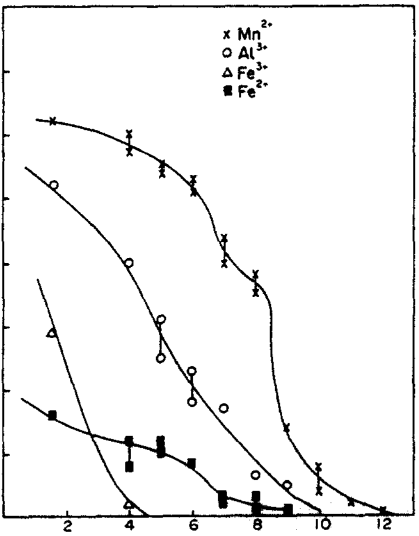


Fig. 2. pH-dependence of the precipitation of Mn^{2+}, Al^{3+}, Fe^{3+} and Fe^{2+} (titration with NaOH).

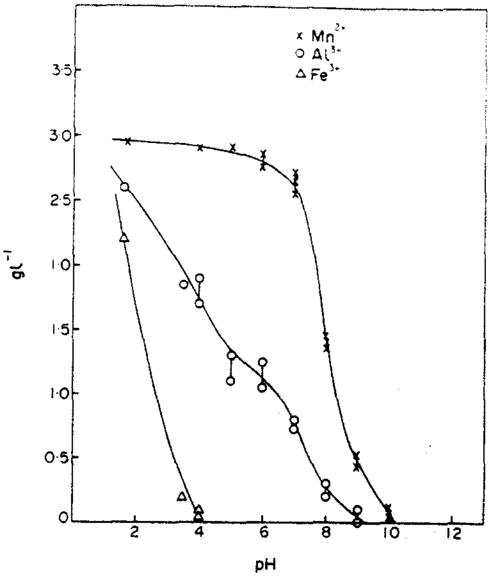


Fig. 3. pH-dependence of the precipitation after oxidation (titration with NaOH).

3. *Ozone*

The oxidation occurs via the overall reaction (Water Pollution Research Series, 1970)

$$2Fe^{2+} + O_3 + 2H^+ \rightarrow 2Fe^{3+} + H_2O + O_2.$$

An important advantage of this reaction is that it follows zero-order kinetics. Theoretically 0·43 g $O_3\,g^{-1}$ of Fe^{2+} is required and experimentally 0·47–0·50 g $O_3\,g^{-1}$ of Fe^{2+} proved to be sufficient for complete oxidation.

In the experiments which led to the results presented in Figs. 2 and 3, NaOH was used to adjust the pH of the solution to the desired value. The same experiments on which Fig. 3 is based, were repeated with $Ca(OH)_2$ as neutralising reagent, the results being given in Fig. 4. As Figs. 3 and 4 are almost identical, various features were studied for a comparison of NaOH and $Ca(OH)_2$ as precipitating reagents.

The neutralisation rate (rate at which the desired pH is reached) was studied at two mixing rates viz. 170 and 900 rev min^{-1}. The results are reported in Fig. 5, from which it follows that the desired pH is reached much faster with NaOH than with $Ca(OH)_2$. This is probably due to the slight solubility of the latter in water. The sedimentation rate was studied by calculating the sedimentation time t_u. According to the method of Talmage and Fitch (1955), t_u is defined as the time required to obtain a certain concentration in the bulk of the sludge. The experimental values are

$$t_u > 60 \text{ min for NaOH}$$

and

$$t_u = 18 \text{ min for } Ca(OH)_2$$

It followed experimentally that $\gamma_{NaOH}:\gamma_{Ca(OH)_2} = 23$, where γ is the specific resistance of the cake (Metcalf

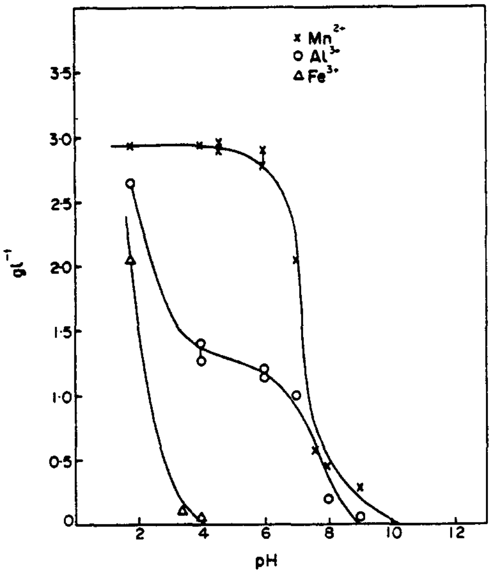


Fig. 4. pH-dependence of the precipitation after oxidation (titration with $Ca(OH)_2$).

and Eddy, 1972). In addition the process of precipitation by $Ca(OH)_2$ is less expensive since $\$_{\mathrm{NaOH}}:\$_{\mathrm{Ca(OH)_2}} \approx 4$. Thus if one takes both economics and quality of precipitate into account, the precipitation process by the addition of $Ca(OH)_2$ is superior even though the precipitation rate is somewhat slower than with NaOH.

To conclude the investigation several experiments were performed to separate the metal ions present. According to the results given in Fig. 3, the oxidised sample could be treated with OH^- to pH 5·0. At this pH, however, Al^{3+} is present in both precipitate and filtrate, while Fe^{3+} precipitates completely and Mn^{2+} remains in solution. This problem can be overcome by adjusting the pH to above 11 where Al^{3+} forms soluble aluminates. Although test solutions of $Al_2(SO_4)_3$ exhibit this probably useful feature, the solubility of aluminates at high hydroxyl concentration could not be improved by any alteration of experimental conditions in the case of the mine effluent. This peculiar behaviour of the Al^{3+} in the effluent is possibly due to the presence of other impurities mentioned before, causing the formation of insoluble aluminates.

A noteworthy modification that indeed improved the separation of the metal ions, is summarized in the following scheme, the results being given in the table below.

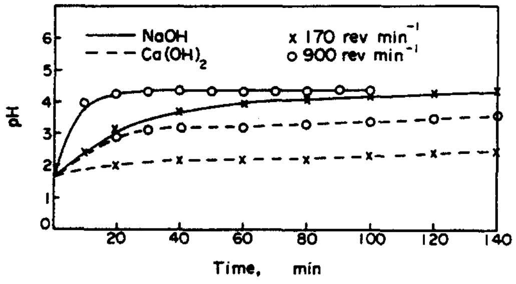
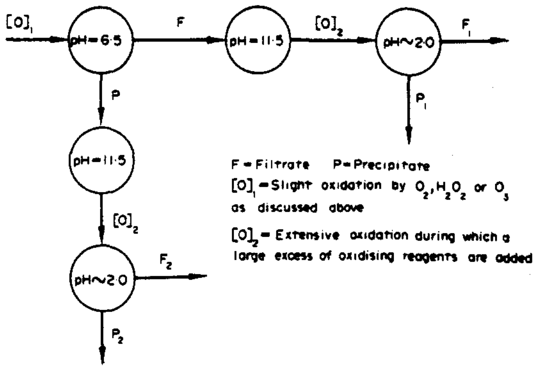


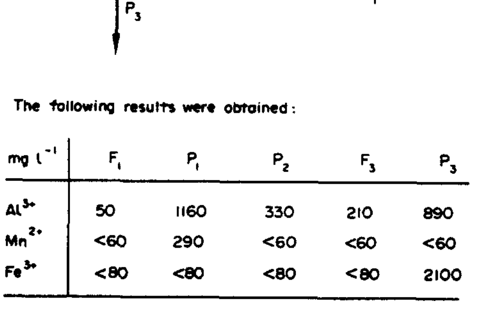
Fig. 5. Comparison of precipitation rate with NaOH and $Ca(OH)_2$.



$mg\,l^{-1}$	F_1	P_1	F_2	P_2
Al^{3+}	<50	730	680	1220
Mn^{2+}	<60	3100	<60	<60
Fe^{3+}	<80	<80	<80	2200

The tabulated values indicate a perfect separation of Fe and Mn, while Al is mainly present in the precipitate at pH 6·5. During the extensive oxidation at pH 11·5 the metal hydroxides are converted to stable oxides which are insoluble even at pH ~ 2·0. This explains why Mn and Fe are present in the precipitates at pH ~ 2·0. The final effluent at pH ~ 2·0 will require further neutralization with lime before it can be discharged. A recycling process of the final precipitate produced in P_2 should improve the separation of Al and Fe considerably.

Another process for the separation of Al^{3+} is summarized in the scheme given below.



The following results were obtained:

$mg\,l^{-1}$	F_1	P_1	P_2	F_3	P_3
Al^{3+}	50	1160	330	210	890
Mn^{2+}	<60	290	<60	<60	<60
Fe^{3+}	<80	<80	<80	<80	2100

The values indicate that some of the Al^{3+} can be recovered, though the results are not as exciting as in the previous scheme. A few alternative methods, including complexation with KCN and the removal of SO_4^{2-} present in the effluent, were investigated (Van der Walt, 1974).

In a nutshell, oxidation of the effluent prior to separation of the metals enables a nearly perfect separation of Fe^{3+} and Mn^{2+}. Both metal fractions, however, still contain Al^{3+} and probably trace quantities of other impurities. It is important to emphasize that once the metals are separated in fractions that only contain Mn^{2+} and Al^{3+} or Fe^{3+} and Al^{3+}, different physical methods are available to complete the separation. At the stated flow rate, approximately 29×10^3 kg day^{-1} Mn, 19×10^3 kg day^{-1} Fe and 25×10^3 kg day^{-1} Al could be recovered as essentially pure compounds. The main expense in the suggested treatment of the effluent is the lime required for the neutralization process. The addition of lime prior to the discharge of the effluent is essential anyway (see Introduction) and is as such an irrecoverable expense. Revenue from the sale of these compounds would cover the treatment costs to a large extent if not fully. This and the peculiar behaviour of Al at high pH seems to justify further investigations preferentially on pilot plant scale.

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