Short communication

Precipitation of sodium silicofluoride (Na$_2$SiF$_6$) and cryolite (Na$_3$AlF$_6$) from HF/HCl leach liquors of alumino-silicates

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The HF + HCl leach liquor generated from the dissolution of silica, alumina and silicate gangue minerals in a low-grade molybdenite concentrate contains H$_2$SiF$_6$ and H$_3$AlF$_6$. Studies were conducted to recover the two valuable fluorides as Na$_2$SiF$_6$ and Na$_3$AlF$_6$ (synthetic cryolite) by precipitation with Na$_2$CO$_3$ from the leach liquor. An initial investigation was carried out to determine the precipitation conditions for Na$_2$SiF$_6$ and Na$_3$AlF$_6$ from their individual acid solutions. Subsequently, the conditions were determined for the selective precipitation of the two fluorides from a synthetic mixed acid solution similar to the leach liquor. When the acid solution was neutralized with 3 mol/L Na$_2$CO$_3$, Na$_2$SiF$_6$ precipitated first at pH 1.35 whilst Na$_3$AlF$_6$ required an increase in pH above 2.2 before it precipitated. Maximum recovery of the two fluorides was best achieved at about 50 °C. A similar trend was observed for the precipitation of Na$_2$SiF$_6$ and Na$_3$AlF$_6$ from the leach liquor of molybdenite upgrading. Phases of precipitated fluorides were identified by XRD and surface morphology by SEM. The purity of the Na$_2$SiF$_6$ precipitate was 99.5% whereas Na$_3$AlF$_6$ was contaminated with Na$_3$FeF$_6$.

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1. Introduction

Low-grade molybdenite concentrates, such as the one available from Jaduguda (India) as a by-product from Uranium Corporation of India Ltd. containing 41.5% Mo, are not suitable for processing unless they are upgraded/concentrated to ≥ 55% Mo. To get such a concentrate, the gangue minerals must be removed by some suitable hydrometallurgical process. Among the various methods considered, the mixture of HF + HCl as a lixiviant is considered potentially useful (Kumar et al., 2007; Mankhand and Prasad, 1982). In the hydrometallurgical process, the leach liquor generated contains H$_2$SiF$_6$ and H$_3$AlF$_6$ because of the dissolution of silica, alumina and silicate gangue. Recovery of the fluorides viz., Na$_2$SiF$_6$ and Na$_3$AlF$_6$ (synthetic cryolite) from the leach liquor contributes not only to the economics of molybdenum upgrading but also aids in the disposal of the final waste solution in an environmentally acceptable manner. Although, a variety of methods are available for the purification and recovery of valuable products from leach liquors, selective precipitation is a suitable simple approach which could be cost effective and environmentally acceptable.

The fluorides such as Na$_3$AlF$_6$ and Na$_2$SiF$_6$ are important industrial chemicals which find diverse applications in metallurgical and chemical industries (Kirk and Othmer, 1966). Industrial production of these chemicals is carried out by appropriate precipitation technologies (Habashi, 1970; Jackson, 1986; Kirk and Othmer, 1966; Simons, 1950). The various processes in vogue for the manufacture of sodium silicofluoride were reviewed by Atochem (1988).

For fluoride recovery as a by-product, Walker (1979) developed a process for recovering fluorine and silicon values from a waste water stream produced in a wet phosphoric acid process. Whilst Habashi and Farouk (1983) removed fluorine and silicon from technical phosphoric acid containing 30% P$_2$O$_5$ by adding sodium or potassium salt, preferably carbonate, and boiling for a few minutes. Therefore, it may be possible to selectively precipitate Na$_3$AlF$_6$ as well as Na$_2$SiF$_6$ by addition of sodium carbonate to leach liquors containing hydrofluosilicic (H$_2$SiF$_6$) and hydrofluoro-aluminic (H$_3$AlF$_6$) acids as per the reactions:

$$H_2SiF_6 + Na_2CO_3 = Na_2SiF_6 + H_2O + CO_2$$

(1)

$$2H_3AlF_6 + 3Na_2CO_3 = 2Na_3AlF_6 + 3H_2O + 3CO_2$$

(2)

In order to devise a procedure for the selective precipitation of Na$_2$SiF$_6$ and Na$_3$AlF$_6$ from complex leach liquors, it is necessary to understand the precipitation conditions for these fluorides from their individual acid solutions using sodium carbonate as precipitant. Subsequently, the conditions need to be determined for the selective precipitation of these two fluorides from a synthetic mixed acid solution similar to the leach liquor. This paper presents the results of
such studies which can be utilized for the removal of aluminosilicate gangue minerals from molybdenite concentrate and other low-grade concentrates and for the recovery of fluoride chemicals.

2. Basis of fluoride precipitation

The conditions applicable for selective precipitation of fluoride chemicals from leach/synthetic solutions can be understood by the theoretical estimation of the solubilities of the fluorides at any pH or fluoride/metal ion concentration.

The dissociation of Na₂SiF₆ can be represented by

\[ \text{Na}_2\text{SiF}_6 \rightleftharpoons 2\text{Na}^+ + \text{SiF}_6^{2-} \]

The log solubility product of Na₂SiF₆ is given by

\[ \log S_1 = 2\log[\text{Na}^+] + \log[\text{SiF}_6^{2-}] \]

Similarly for dissociation of Na₃AlF₆

\[ \text{Na}_3\text{AlF}_6 \rightleftharpoons 3\text{Na}^+ + \text{AlF}_3^{3-} \]

The log solubility product of Na₃AlF₆ is given by

\[ \log S_2 = 3\log[\text{Na}^+] + \log[\text{AlF}_3^{3-}] \]

where \( S_1 \) and \( S_2 \) are the solubility products of Na₂SiF₆ and Na₃AlF₆ (1 \times 10^{-6} and 4 \times 10^{-10}, respectively).

3. Materials and methods

3.1. Materials

The leach liquor generated during the refining of the low-grade Jaduguda molybdenite concentrate was analysed and the composition is given in Table 1. The initial pH of the leach solution was determined to be 0.60. The synthetic solutions were prepared from reagent grade chemicals.

3.2. Methods

Standard synthetic solutions of H₂SiF₆ and H₃AlF₆ were prepared by dissolving silica gel and active alumina, respectively in aqueous HF. Since the rate of dissolution of alumina in hydrofluoric acid was very slow, it was carried out at 100 °C in a 200 ml PTFE lined autoclave. Precipitation experiments were conducted by adding alkaline precipitant gradually from a burette to the 50 mL acid solution with pH adjustment by conc. HCl. It was observed that use of 1 mol/L Na₂CO₃ gradually from a burette to the 50 mL acid solution with pH 1.35.

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The maximum precipitation efficiency of 97.4% Na₂SiF₆ was obtained after 0.5 h. from 0.16 mol/L H₂SiF₆ when the solution was neutralized to pH 5.0 at 80 °C using excess 1 mol/L Na₂CO₃. In the case of 0.06 mol/L H₃AlF₆, 97.5% Na₃AlF₆ was precipitated at 70 °C and pH 4.0 after 0.5 h. The addition of 'seed' (Na₂SiF₆ or Na₃AlF₆) prior to precipitation was found to be beneficial to achieve enhanced recovery.

4. Results and discussion

4.1. Precipitation from individual acid solutions

Initially, investigations were carried out to understand the precipitation behavior of Na₂SiF₆ and Na₃AlF₆ using 1 mol/L Na₂CO₃ to neutralize the individual synthetic solutions of H₂SiF₆ (0.1–0.5 mol/L) and H₃AlF₆ (0.06–0.09 mol/L), respectively. In both the cases the effect of pH and temperature on precipitation was studied and the phases in the precipitates were identified by XRD. It was observed that single phase fluorides precipitated with excess Na₂CO₃ up to pH 4 and 5, beyond which Na₂SiF₆ was contaminated with sodium silicate (Na₂SiO₅) while Na₃AlF₆ was contaminated with chiolite (Na₅Al₃F₁₄).

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4.2. Precipitation of Na₂SiF₆ from the mixed acid solution

Similar experiments were conducted with a mixed synthetic (model) solution of 0.32 mol/L H₂SiF₆ and 0.06 mol/L H₃AlF₆ to test the pattern of selective precipitation of Na₂SiF₆ using 3 mol/L Na₂CO₃ solution.

The precipitation efficiency of Na₂SiF₆, determined in a pH range 0.95 to 1.35 is depicted in Fig. 1. It is seen that almost complete precipitation was obtained at pH 1.35 and 30 °C in 2 h time using stoichiometric quantity of 3 mol/L Na₂CO₃. In order to get more precipitation of Na₂SiF₆, a 40% excess of 3 mol/L Na₂CO₃ was added, taking the pH above 1.35, but the chemical analysis of the product (Na₂SiF₆) showed that it was contaminated with Na₃AlF₆. Precipitation would undoubtedly be favored by additional sodium ion due to the common ion effect on solubility. The literature value for the solubility of Na₂SiF₆ is 9.40 g/L in water at 25 °C and 24.50 g/L in water at 100 °C (Stephen and Stephen, 1962).

4.3. Precipitation of Na₃AlF₆ from silicon depleted mixed acid solution

The solution left after the precipitation of Na₂SiF₆ was used for the recovery of synthetic cryolite (Na₃AlF₆) by adding further 3 mol/L Na₂CO₃ solution in excess of 200% over the stoichiometric requirement, taking the pH up to pH 4.0. The results of the effect of excess Na₂CO₃, and hence increased pH, on precipitation efficiency show that Na₃AlF₆...
recovery increased from 51% to 75% (Fig. 2). The influence of temperature (30–75 °C) at pH 4.0 on the precipitation efficiency of Na3AlF6 showed that the recovery of Na3AlF6 reached a maximum at 55 °C and then decreased with further increases in temperature. The literature solubility of Na3AlF6 is 0.61 g/L in water at 25 °C and 2.72 g/L in water at 100 °C (Stephen and Stephen, 1962). At 55 °C, it appears that the activity of sodium ion is higher and it was possible to recover about 95% Na3AlF6 from the solution in 1 h (Fig. 3).

4.4. Precipitation of fluorides from molybdenite leach liquor

The applicability of the above results conducted for the recovery of Na2SiF6 and Na3AlF6 from synthetic mixed acid solution was then examined for the actual leach liquor containing 0.32 mol/L H2SiF6, 0.06 mol/L H3AlF6, 0.046 mol/L Fe and minor amounts of copper and nickel (Table 1) obtained from the refining of the low-grade molybdenite concentrate.

The effect of pH on the recovery of Na2SiF6 was again studied, using 3 mol/L Na2CO3 to neutralize the acids. A similar trend to that of the synthetic acid mixture was observed (Fig. 1) almost complete recovery of Na2SiF6 was achieved at pH 1.50 using 110% excess Na2CO3. The purity of Na2SiF6 recovered was found to be over 99.5% at pH 1.35 with minor amounts of aluminium (0.2%) and iron (0.3%) as the impurities.

The filtrate after the precipitation of Na2SiF6 was used for the recovery of Na3AlF6. Increasing the excess Na2CO3 and pH beyond 1.50 showed the precipitation of an iron(III) compound contaminating the cryolite, especially at around pH 2.2. The XRD study of the compounds precipitated at this pH indicated the contaminant was sodium ferric-fluoride (Na3FeF6). This calls for the removal of iron(III) by solvent extraction (Ritcey and Ashbrook, 1984) to avoid iron contamination in Na3AlF6. Although it may be possible to remove iron contamination in Na3AlF6 by fractional re-precipitation.

4.5. Surface morphology

The scanning electron micrograph (SEM) of selectively precipitated sodium silico-fluoride at pH 1.35 from the mixed synthetic solutions of hydrofluoro-silicic acid and hydrofluoro-aluminic acid is shown in Fig. 4. The sodium silico-fluoride was found to have a rectangular shape (2–3 μm size) with some particles agglomerated. The SEM of sodium silico-fluoride precipitated from the leach liquor at pH 1.50 was very similar in shape and size. SEM–EDS studies indicated the presence of minor amounts of aluminium in the sodium silico-fluoride from the mixed synthetic solution, whereas no aluminium was detected in Na2SiF6 from the leach liquor.

5. Conclusions

I. From individual acid solutions of H2SiF6 and H3AlF6, both Ni2SiF6 and Na3AlF6 could be precipitated by adding excess Na2CO3 up to pH 5.0 and 4.0, beyond which they are contaminated with other phases such as sodium silicate and chiolite respectively.

II. From the mixed acid solution, Na2SiF6 was found to precipitate before Na3AlF6. Almost complete precipitation of Na2SiF6 was achieved by stoichiometric addition of Na2CO3 at pH 1.35. Further addition of Na2CO3 and increase in pH above 1.35 resulted in the precipitation of Na3AlF6.

III. The maximum recovery of both fluorides was achieved at about 50 °C beyond which the solubility of the precipitated fluorides increases.

IV. Similar results were obtained for the precipitation of Na2SiF6 and Na3AlF6 from the leach liquors of low-grade molybdenite containing aluminosilicates. The near complete recovery of Na2SiF6 with 99.5% purity was obtained from the leach liquor at pH 1.50 using 3 mol/L Na2CO3. The SEM–EDS of Na2SiF6 shows irregular rectangular shaped particles of 2–3 μm size with the
tendency of agglomeration. The cryolite was found to be contaminated with sodium ferric–fluoride.

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