



Short communication

Precipitation of sodium silicofluoride (Na_2SiF_6) and cryolite (Na_3AlF_6) from HF/HCl leach liquors of aluminosilicates

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ABSTRACT

The HF + HCl leach liquor generated from the dissolution of silica, alumina and silicate gangue minerals in a low-grade molybdenite concentrate contains H_2SiF_6 and H_3AlF_6 . Studies were conducted to recover the two valuable fluorides as Na_2SiF_6 and Na_3AlF_6 (synthetic cryolite) by precipitation with Na_2CO_3 from the leach liquor. An initial investigation was carried out to determine the precipitation conditions for Na_2SiF_6 and Na_3AlF_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_2CO_3 , Na_2SiF_6 precipitated first at pH 1.35 whilst Na_3AlF_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_2SiF_6 and Na_3AlF_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_2SiF_6 precipitate was 99.5% whereas Na_3AlF_6 was contaminated with Na_3FeF_6 .

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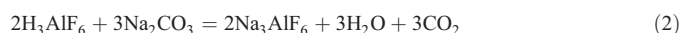
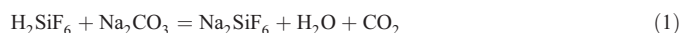
1. Introduction

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 $\geq 55\%$ 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_2SiF_6 and H_3AlF_6 because of the dissolution of silica, alumina and silicate gangue. Recovery of the fluorides viz., Na_2SiF_6 and Na_3AlF_6 (synthetic cryolite) from the leach liquor contributes not only to the economics of molybdenite 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_3AlF_6 and Na_2SiF_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_2O_5 by adding sodium or potassium salt, preferably carbonate, and boiling for a few minutes. Therefore, it may be possible to selectively precipitate Na_3AlF_6 as well as Na_2SiF_6 by addition of sodium carbonate to leach liquors containing hydrofluosilicic (H_2SiF_6) and hydrofluo-aluminic (H_3AlF_6) acids as per the reactions:



In order to devise a procedure for the selective precipitation of Na_2SiF_6 and Na_3AlF_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

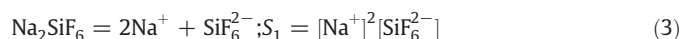
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such studies which can be utilized for the removal of alumino-silicate gangue minerals from molybdenite concentrate and other low-grade concentrates and for the recovery of fluoride chemicals.

2. Basis of fluoride precipitation

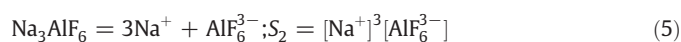
The conditions applicable for selective precipitation of fluoride chemicals from leach/synthetic solutions can be understood by the theoretical estimation of the solubilities of the fluorides at any pH or fluoride/metal ion concentration.

The dissociation of Na_2SiF_6 can be represented by



$$\log S_1 = 2 \log[\text{Na}^+] + \log[\text{SiF}_6^{2-}] \quad (4)$$

Similarly for dissociation of Na_3AlF_6



$$\log S_2 = 3 \log[\text{Na}^+] + \log[\text{AlF}_6^{3-}] \quad (6)$$

where S_1 and S_2 are the solubility products of Na_2SiF_6 and Na_3AlF_6 (1×10^{-6} and 4×10^{-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 H_2SiF_6 and H_3AlF_6 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 Na_2CO_3 diluted the filtrate too much for the recovery of Na_3AlF_6 . Hence 3 mol/L Na_2CO_3 was used for the precipitation of both Na_2SiF_6 and Na_3AlF_6 from the mixed acid solutions as well as from the leach liquor of molybdenite processing.

In these experiments, the precipitate was allowed to settle and then filtered, washed, and dried for over 2 h at 110 °C in oven. From the weight of the dried precipitate obtained, the precipitation efficiency was calculated. Phases present in the precipitates were identified by XRD (Phillips, Model Xpertro). Chemical analysis of leach liquor was carried out by Atomic Absorption Spectrometer (UNICAM, Model Solar). The scanning electron micrographs were also taken for some precipitated samples.

Table 1

Composition of the leach liquor generated from molybdenite concentrate. Leaching condition: 5 wt.% (HCl + HF); 25% excess acids; stirred at 1500 rpm; solid/liquid ratio: 200 g/L; 120 °C.

	Mo	S	Si*	Al*	Fe	Cu	Ni
% in Mo con. (*as oxides)	41.5	30.2	9.6	1.6	2.93	0.36	0.27
mol/L in leach solution			0.32	0.06	0.046	0.0041	0.0036

4. Results and discussion

4.1. Precipitation from individual acid solutions

Initially, investigations were carried out to understand the precipitation behavior of Na_2SiF_6 and Na_3AlF_6 using 1 mol/L Na_2CO_3 to neutralize the individual synthetic solutions of H_2SiF_6 (0.1–0.5 mol/L) and H_3AlF_6 (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 Na_2CO_3 up to pH 4 and 5, beyond which Na_2SiF_6 was contaminated with sodium silicate (Na_2SiO_5) while Na_3AlF_6 was contaminated with chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$). The maximum precipitation efficiency of 97.4% Na_2SiF_6 was obtained after 0.5 h. from 0.16 mol/L H_2SiF_6 when the solution was neutralized to pH 5.0 at 80 °C using excess 1 mol/L Na_2CO_3 . In the case of 0.06 mol/L H_3AlF_6 , 97.5% Na_3AlF_6 was precipitated at 70 °C and pH 4.0 after 0.5 h. The addition of 'seed' (Na_2SiF_6 or Na_3AlF_6) prior to precipitation was found to be beneficial to achieve enhanced recovery.

4.2. Precipitation of Na_2SiF_6 from the mixed acid solution

Similar experiments were conducted with a mixed synthetic (model) solution of 0.32 mol/L H_2SiF_6 and 0.06 mol/L H_3AlF_6 to test the pattern of selective precipitation of Na_2SiF_6 using 3 mol/L Na_2CO_3 solution.

The precipitation efficiency of Na_2SiF_6 , 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 Na_2CO_3 . In order to get more precipitation of Na_2SiF_6 , a 40% excess of 3 mol/L Na_2CO_3 was added, taking the pH above 1.35, but the chemical analysis of the product (Na_2SiF_6) showed that it was contaminated with Na_3AlF_6 . Precipitation would undoubtedly be favored by additional sodium ion due to the common ion effect on solubility. The literature value for the solubility of Na_2SiF_6 , 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 Na_3AlF_6 from silicon depleted mixed acid solution

The solution left after the precipitation of Na_2SiF_6 was used for the recovery of synthetic cryolite (Na_3AlF_6) by adding further 3 mol/L Na_2CO_3 solution in excess of 200% over the stoichiometric requirement, taking the pH up to pH 4.0. The results of the effect of excess Na_2CO_3 , and hence increased pH, on precipitation efficiency show that Na_3AlF_6

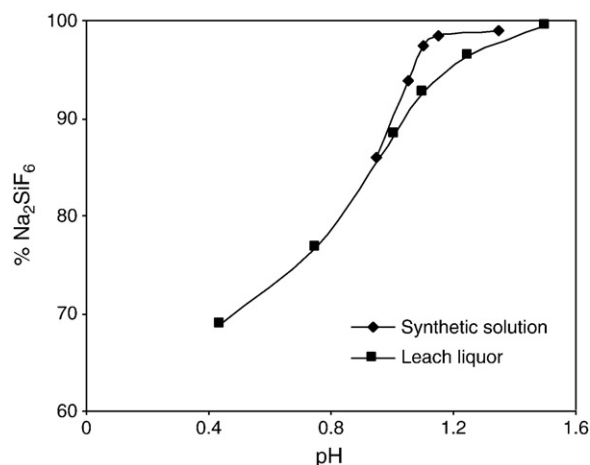


Fig. 1. Effect of pH on the precipitation of sodium silicofluoride from the mixed acid synthetic solution (0.32 mol/L H_2SiF_6 + 0.06 mol/L H_3AlF_6) and leach liquor [Precipitant: 3 mol/L Na_2CO_3 , t: 2 h, temp.: 30 °C].

recovery increased from 51% to 75% (Fig. 2). The influence of temperature (30–75 °C) at pH 4.0 on the precipitation efficiency of Na_3AlF_6 showed that the recovery of Na_3AlF_6 reached a maximum at 55 °C and then decreased with further increases in temperature. The literature solubility of Na_3AlF_6 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% Na_3AlF_6 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 Na_2SiF_6 and Na_3AlF_6 from synthetic mixed acid solution was then examined for the actual leach liquor containing 0.32 mol/L H_2SiF_6 , 0.06 mol/L H_3AlF_6 , 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 Na_2SiF_6 was again studied, using 3 mol/L Na_2CO_3 to neutralize the acids. A similar trend to that of the synthetic acid mixture was observed (Fig. 1) almost complete recovery of Na_2SiF_6 was achieved at pH 1.50 using 110% excess Na_2CO_3 . The purity of Na_2SiF_6 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 Na_2SiF_6 was used for the recovery of Na_3AlF_6 . Increasing the excess Na_2CO_3 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 (Na_3FeF_6). This calls for the removal of iron(III) by solvent extraction (Ritcey and Ashbrook, 1984) to avoid iron contamination in Na_3AlF_6 . Although it may be possible to remove iron contamination in Na_3AlF_6 by fractional re-precipitation.

4.5. Surface morphology

The scanning electron micrograph (SEM) of selectively precipitated sodium silicofluoride at pH 1.35 from the mixed synthetic solutions of hydrofluoro-silicic acid and hydrofluoro-aluminic acid is shown in Fig. 4. The sodium silicofluoride was found to have a rectangular shape (2–3 μm size) with some particles agglomerated. The SEM of sodium silicofluoride 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 silicofluoride from the

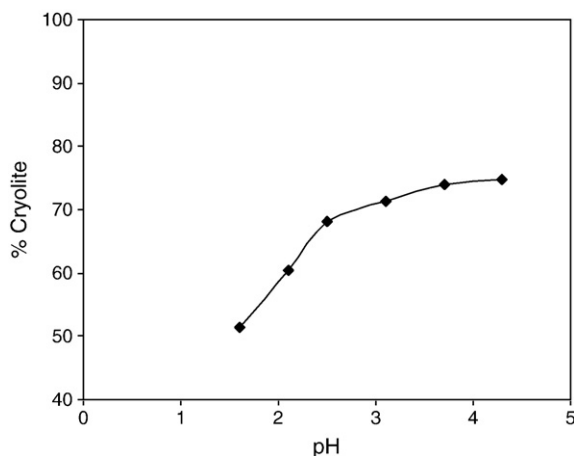


Fig. 2. Effect of pH on the recovery of cryolite from silicon depleted mixed acid solution (0.03 mol/L H_2SiF_6 + 0.06 mol/L H_3AlF_6) [Precipitant: 3 mol/L Na_2CO_3 (200% excess), temp: 30 °C, t: 1 h].

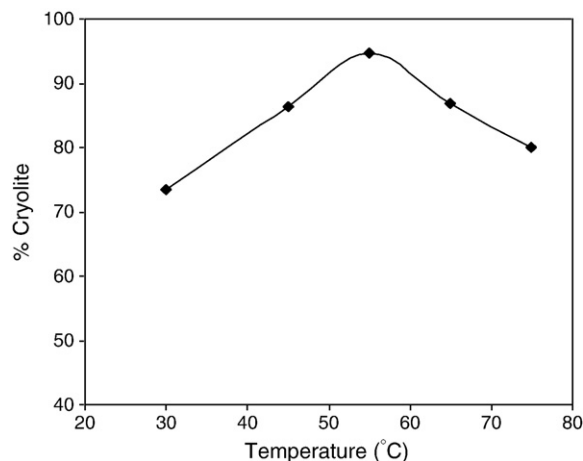


Fig. 3. Effect of temperature on the precipitation of cryolite from the depleted mixed acid solution [Precipitant: 3 mol/L Na_2CO_3 (200% excess), pH: 4.0, t: 1 h].

mixed synthetic solution, whereas no aluminium was detected in Na_2SiF_6 from the leach liquor.

5. Conclusions

- I. From individual acid solutions of H_2SiF_6 and H_3AlF_6 , both Ni_2SiF_6 and Na_3AlF_6 could be precipitated by adding excess Na_2CO_3 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, Na_2SiF_6 was found to precipitate before Na_3AlF_6 . Almost complete precipitation of Na_2SiF_6 was achieved by stoichiometric addition of Na_2CO_3 at pH 1.35. Further addition of Na_2CO_3 and increase in pH above 1.35 resulted in the precipitation of Na_3AlF_6 .
- 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 Na_2SiF_6 and Na_3AlF_6 from the leach liquors of low-grade molybdenite containing aluminosilicates. The near complete recovery of Na_2SiF_6 with 99.5% purity was obtained from the leach liquor at pH 1.50 using 3 mol/L Na_2CO_3 . The SEM–EDS of Na_2SiF_6 shows irregular rectangular shaped particles of 2–3 μm size with the

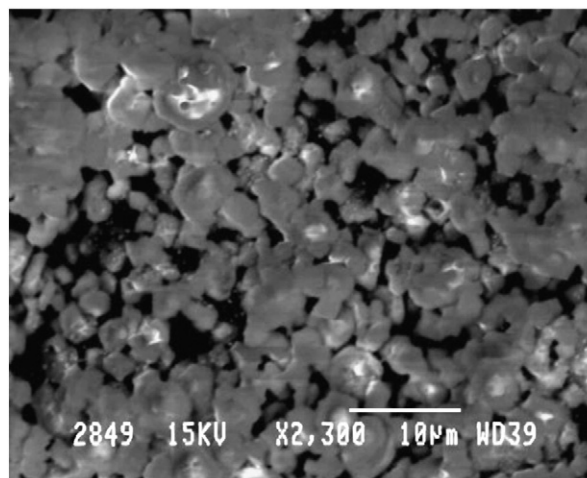


Fig. 4. SEM photograph of the sodium silicofluoride precipitated from the mixed acid at pH 1.35.

tendency of agglomeration. The cryolite was found to be contaminated with sodium ferric-fluoride.

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References

- Atochem, J.P.C., 1988. Fluorine compounds, inorganic, In: Gerhartz, W. (Ed.), Fifth Edition. Ullmann's Encyclopedia of Industrial Chemistry, vol. A-11. VCH Weinheim, Germany, pp. 332–337.
- Habashi, F., 1970. Principles of extractive metallurgy. Hydrometallurgy, vol. 2. Gordon & Breach, New York.
- Habashi, F., Farouk, A.T., 1983. Removal of fluorine from wet process phosphoric acid. Separation Science and Technology 18 (5), 485–491.
- Jackson, E., 1986. Hydrometallurgical Extraction and Reclamation. Ellis Horwood Ltd., West Sussex, UK.
- Kirk, R., Othmer, D.F., 1966. Fluorine compounds, inorganic. In: Parolla, Eva A. (Ed.), Encyclopedia of Chemical Technology, Vol. 9. Wiley-Interscience, New York, pp. 535–548.
- Kumar, M., Mankhand, T.R., Murthy, D.S.R., Mukhopadhyay, R., Prasad, P.M., 2007. Refining of a low-grade molybdenite concentrate. Hydrometallurgy 86 (1–2), 56–62.
- Mankhand, T.R., Prasad, P.M., 1982. Lime enhanced hydrogen reduction of molybdenite. Metallurgical Transactions 13B, 275–282.
- Ritcey, G.M., Ashbrook, A.W., 1984. Solvent Extraction Part I. Principles and Applications to Process Metallurgy. Elsevier, New York.
- Simons, J.H., 1950. The chemistry of the fluoro acids of fourth, fifth and sixth group elements. In: Lange, Willy (Ed.), Fluorine Chemistry, Vol. 1. Academic Press Inc, New York.
- Stephen, H., Stephen, T., 1962. Solubility of Inorganic and Organic Compounds. Pergamon Press, London.
- Walker, T. F., 1979. Process for the simultaneous production of wet process phosphoric acid and sodium silicofluoride, U. S. Patent No. 4,178,347.