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Distillation of Hydrofluoric Acid from Acid Fluoride-Sulphate Solutions

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Abstract

The paper describes distillation of hydrofluoric acid from model and process acid fluoride-sulphate solutions. Conditions for the most complete distillation of hydrofluoric acid from fluoride-sulphate solutions were determined and proposed. Fluorosulphonic acid is formed in large amounts, as shown for model solutions containing hydrofluoric and sulphuric acids. Herewith, with increasing the concentration of acids, their interaction degree rises and fluorosulphonic acid is formed, as demonstrated. An increase in the heating temperature of the mixture leads to a substantial increase in acidity due to HSO_3F content decrease. The larger the concentration of acids (especially, sulphuric) is, the higher heating temperatures are required to decompose HSO_3F , as established. The formation of fluorosulphonic acid may have a significant effect on HF distillation degree, as shown. The energetic and economic cost in the processing of 1 m³ of process acid fluoride-sulphate solution is calculated with an account of the initial concentration of HF of 78 g/L. Considering sulphuric acid regeneration and having excluded lime content for its neutralization, energy costs for processing of this solution do not exceed 4500 RUB. The findings explain high solubility of lanthanide fluorides compared to their dissolution in monobasic acids, as noted in a series of papers. Our earlier observations of decreasing the concentration of fluorine determinable by potentiometric titration relatively to initially introduced one at pH correction by using sulphuric acid, unlike that with nitric or hydrochloric ones were also explained.

Keywords: hydrofluoric acid, fluoride-sulphate solutions, fluorosulphonic acid, distillation

INTRODUCTION

Fluoride-sulphate solutions are formed in large volumes by sulphuric acid technology during the complex processing of rare earth concentrates containing titanium, niobium, and tantalum [1]. These solutions are also formed during fluoride-sulphuric processing of columbite or tantalite after extraction isolation of niobium and tantalum [2–4]. The resulting solutions are neutralized with lime; SO_4^{2-} and F^- anions are precipitated as CaSO_4 and CaF_2 and sent for disposal [2–4].

The relevance of isolating hydrofluoric acid from fluoride-sulphate solutions and its use in the turnover is obvious and driven by not only environmental expediency but also significant economic benefits. Thus, for example, the cost 40 % technical hydrofluoric acid is approximately 55 RUB /kg, that of technical sulphuric acid – 5–11 RUB/kg [5].

Fluorine distillation from the resulting fluoride-sulphate solutions using silica enables extraction of nearly 97 % of fluorine as SiF_4 [6]. However, the classic distillation methods of fluorine distillation as SiF_4 involve

instrumentation complexity and significant time costs [7]. Additionally, fluorine should be transformed to HF from SiF_4 , which requires the introduction of additional production stages.

The problem can seemingly be solved *via* direct HF distillation from solutions of this sort. However, during HF distillation from fluoride-sulphate solutions, fluorosulphonic acid (HSO_3F) is formed therein. Earlier (*e.g.* [6]), this fact was not taken into account, however, it may complicate distillation of hydrofluoric and sulphuric acid solutions.

Thus, there is still no common and comprehensive idea of interaction processes and conditions of distillation of components from fluoride-sulphate solutions [7].

It is known [8] that in industry fluorosulphonic acid is obtained by the interaction of SO_3 with HF. It may also be produced by the following methods: distillation of mixtures of KHF_2 and NH_4F , CaF_2 and oleum, fluorosulphonates and concentrated sulphuric acid; the introduction of chlorosulphonic acid into liquid hydrogen fluoride [8].

Softer conditions may also yield HSO_3F . Thus, it is formed in significant amounts during mixing concentrated sulphuric and ~37 % hydrofluoric acid, according to [9].

Increasing H_2SO_4 contents in the HF- H_2SO_4 - H_2O system contributes to the formation of HSO_3F . At the same time, HSO_3F contents in solutions decrease and approach zero with increasing HF and H_2O content in a mixture of more than 0.2 and 1.0 mole, respectively (Fig. 1).

Decomposition of CaF_2 by H_2SO_4 at 85, 95 or 100 °C yields fluorosulphonic acid, while relatively fast and almost complete decomposition of HSO_3F may proceed in the 105–145 °C temperature range, as presumed by the authors of [10].

An increase in H_2SO_4 concentration for solutions with identical initial concentrations of hydrofluoric acid leads to a reduction in HF vapour pressure above the solution. This fact is explained by the formation of fluorosulphonic acid that is more resistant in concentrated solutions of sulphuric acid [11].

The total vapour pressure above solutions in the HF- H_2SO_4 - H_2O system increases with rising temperature and HF contents in the initial mixture, and water content increase and

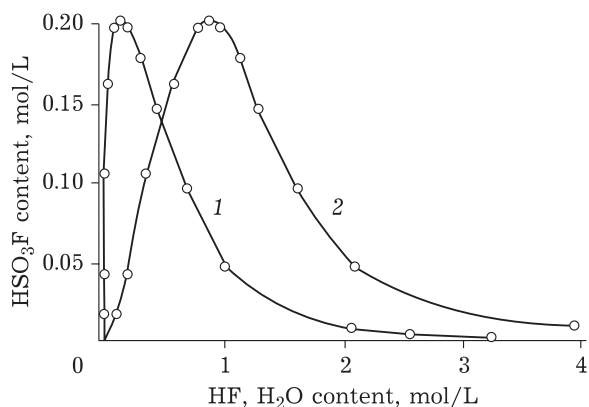


Fig. 1. Effect of HF (1) and H_2O (2) content in the HF- H_2SO_4 - H_2O system on the formation of fluorosulphonic acid [9]. H_2SO_4 content is 1 mol/L, $T = 24^\circ\text{C}$.

H_2SO_4 content decrease in the liquid phase at the equal hydrogen fluoride content in the initial solution contribute to increasing the total vapour pressure [12].

At the same time, it is alleged in [8] that fluorosulphonic acid is resistant at temperatures up to 163 °C; its boiling point is 162.6 °C.

Distillation of hydrofluoric acid in paper [13] was carried out from raffinate obtained after extraction of niobium and tantalum, distillation of acid fluoride solution up to a concentration of fluoride ions of 300 g/L and its strengthening with concentrated (92 %) sulphuric acid to reach a concentration against H_2SO_4 of 1000–1100 g/L. Process temperature was maintained within 110–120 °C. About 90 % of hydrofluoric acid was isolated resulting from distillation from the raffinate. The content of sulphate ions in the distillate was unspecified. Still residue was headed for crystallization of titanyl sulphate monohydrate by heating with direct steam to a temperature of 140–150 °C. The remaining mother liquid contained concentrated sulphuric acid (1200–1300 g/L) and residual HF (10 %). The disadvantage of this method is the need for preliminary raffinate distillation. The authors of [13] did not provide reasons for incomplete distillation of HF from the raffinate with high HF and H_2SO_4 content.

The work purpose was the study of an opportunity and conditions for complete distillation of hydrofluoric acid from fluoride-sulphate solutions.

The effect of the concentration of acids (HF and H_2SO_4) and temperature on the formation

of fluorosulphonic acid was studied within the framework of the goal set.

EXPERIMENTAL

To study the dependence of the formation of fluorosulphonic acid on component concentration a mixture of acid solutions with calculated HF and H₂SO₄ content was prepared.

The ratio of acid concentrations in model solutions corresponds to that in the most used process solutions. Chemically pure hydrofluoric (45 mass %) and sulphuric (93 mass %) acids were selected as initial reagents. Distilled water was used to prepare solutions. The prepared solutions simultaneously contained both acids in the amount of 0.8–6 mol/L.

RESULTS AND DISCUSSION

The solution temperature was increased depending on acid concentration in mixtures under preparation during solution production by mixing of initial reagents containing calculated acid concentrations.

After cooling, the total volume of the solution corresponded to the volume of the fused solutions. Immediately after preparation of working solutions and their cooling to 20°C, the concentration of the acids was determined by titration (according to the indicator methyl orange). These solutions were heated to 110–120°C and then also titrated. The results are presented Table 1.

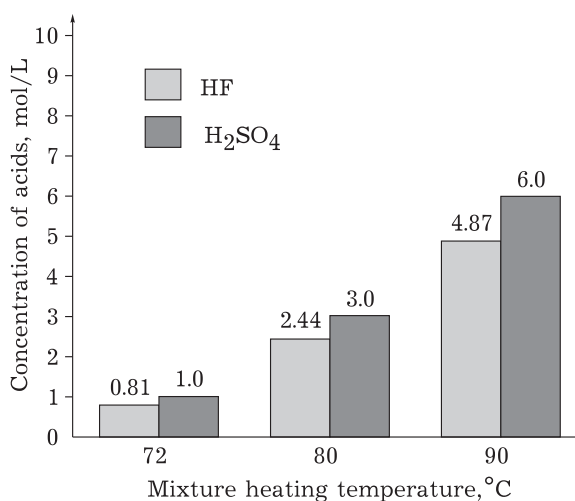


Fig. 2. Heating temperature of the mixture vs. the concentration of acids being mixed (HF and H₂SO₄).

Formation of fluorosulphonic acid

It can be seen that heating to 72–90°C happens during mixing of acids depending on their concentration in solutions (Fig. 2). Herewith, acid concentrations for all operating solutions determinable after cooling to 20°C are lower than their calculated values, *i.e.* there is a decrease in acidity (C_{H+}).

The observable difference between calculated and actual values of acidity for the resulting fluoride-sulphate solutions is related to the formation of HSO₃F by the reaction:

$$\text{H}_2\text{SO}_4 + \text{HF} \rightarrow \text{HSO}_3\text{F} + \text{H}_2\text{O} \quad (1)$$

According to reaction (1), the equimolar interaction of HF with H₂SO₄ that yields fluorosulphonic acid leads to a decrease in the

TABLE 1

Titration results of solutions of HF and H₂SO₄ acids

Растворы	Calculated C in the mixture, mol/L		Total C _{H+} in the mixture, g-equiv/L	Temperature pre-heating, °C	Total actual C _{H+} in the mixture, g-equiv/L	Acidity decrease, g-equiv/L
	HF	H ₂ SO ₄				
1	0.81	1	2.81	72	2.70	0.11
				110	2.81	0
2	2.44	3	8.44	80	7.79	0.65
				110	7.93	0.51
3	4.87	6	16.87	90	16.30	0.57
				110	15.79	1.08

concentration of protons in 3 times, that is acidity decrease in the formation of x moles of HSO_3F is $2x$ moles.

Heating to a temperature of 110°C with a sulphuric acid concentration in fluoride-sulphate solution of less than 4 mol/L contributes to a decrease in the concentration of HSO_3F that completely or partially decomposes to initial components (HF and H_2SO_4). This leads to a significant increase of solution acidity (Table 1).

Unlike the first two solutions for solution No 3 (see Table. 1) with a substantially higher initial concentration of sulphuric acid, the acidity is reduced, indicating the formation of an additional amount of HSO_3F in this temperature range of $90\text{--}110^\circ\text{C}$.

Hydrolysis processes become intensified when increasing water content in the solution and its heating temperature leading to the destruction of fluorosulphonic acid. On the contrary, increasing the sulphuric acid concentration suppresses the hydrolytic processes and contributes to the formation of HSO_3F .

This is related to increasing the concentration of hydrogen ions. Fluoride ion is likely to replace one of the acid OH groups in a molecule of sulphuric acid, and the OH group from a molecule of sulphuric acid, adding a proton, transforms into water.

The diagram of boiling of sulphuric acid solutions demonstrates [14] that during heating a solution with the H_2SO_4 content of less than

80% (14.1 mol/L), the boiling point is below 200°C , herewith, only water passes into vapours. The H_2SO_4 content in vapours significantly increases just in case of a solution with H_2SO_4 concentration of above 93% (17.3 mol/L), the boiling point of which exceeds 290°C . A gas-vapour mixture of HF and H_2O instead of water should be released during heating of acid fluoride-sulphate solutions.

Proceeding from the above, an increase in heating temperature of the solution should lead to decomposition of HSO_3F also at high concentrations of sulphuric acid.

A high temperature of heating the mixture that should increase to 160°C and higher is likely to be required for efficient distillation of HF from fluoride-sulphate solutions. In other words, the complete distillation of HF from such solutions should be carried out at temperatures that exceed the boiling point of HSO_3F .

Distillation of HF from model fluoride-sulphate solutions

Distillation of HF at high temperatures was carried out from the model solution containing 72.5 g/L of HF and 404 g/L of H_2SO_4 .

A distillation setup for evaporation of hydrogen fluoride is presented in Fig. 3.

A solution was placed into a hermetically sealed fluoroplastic glass that was lowered into a sand bath placed over a furnace of the open

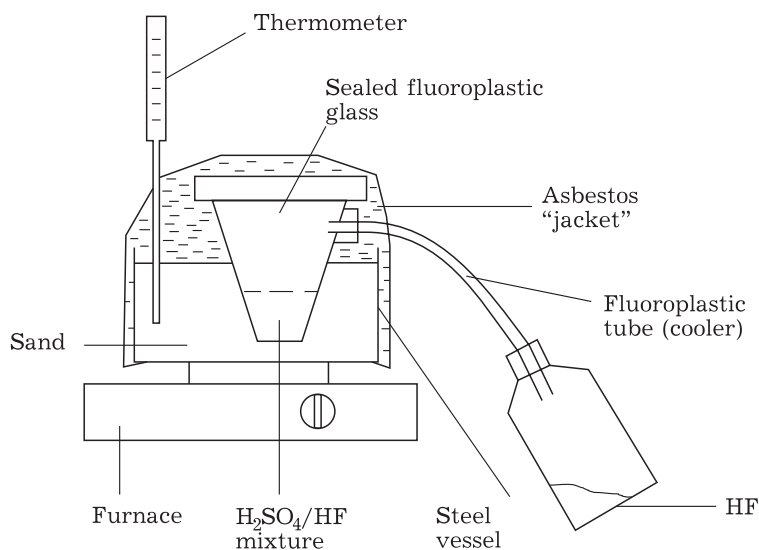


Fig. 3. Scheme of the distillation setup for hydrogen fluoride distillation from fluoride-sulphate solution.

type. To monitor temperature a thermometer immersed into sand onto a height of fluoroplastic glass was used. The temperature inside the glass was maintained within 170–190 °C. The difference between the temperature in the sand bath and that inside the fluoroplastic glass with a fluoride-sulphuric acid solution was on average 30 °C.

Only water vapours and hydrogen fluoride are distilled off at these temperatures [14]. It was condensed in the amount of 95.17 % during distillation. The content of H_2SO_4 in the distillate is negligible (0.2 %).

The residue is a concentrated H_2SO_4 solution, in which fluorine content is 0.77 % of the initial amount. Evidently, losses due to instrumentation imperfection determine 4.06 % of fluorine undefined in the residue. The time spent on heating and distillation was 6–7 h.

Thus, it was possible to capture over 95 % of hydrofluoric acid.

Distillation of HF from process fluoride-sulphate solutions

The process solution of processing of rare-earth titanoniobates, from which distillation of HF was carried out has the following composition, mg/L: Nb 91.6, Ta 0.58, Zr 166.2, Al 417.5, Ti 1320, Fe 13490, Si 3300, Ca 74.08, Sn 216.4, W 507.2, Mn 1860, F 78 000, SO_4 340 760.

The results of distillation of HF from the process solution for processing of rare-earth titanoniobates demonstrated that it was possible to distill and capture only 78 % of HF initial content in the solution.

As water evaporates, the concentration of sulphuric acid increases, therefore, the temperature increase is required for complete distillation of HF from this mixture. It is assumed that an increase in the distillation temperature to 180–250 °C will contribute to more complete release of HF from a fluoride-sulphate solution.

Thus, over 90 % of fluorine of the initial content was transferred of the distillate to form a solution with the concentration of HF of 105.3 g/L. The content of sulphuric acid in the distilled solution was 0.54 % of its initial content.

Less than 1 % of fluorine was detected in the residue of the initial solution after distillation. Disbalance for fluorine between the distilled

solution and the residue is 9 %, which may be related to construction flaws in process instrumentation.

According to X-ray phase and crystallographic analysis, a precipitate formed after distillation represents sulphate iron compounds (the main phase is rhomboclase $(H_5O_2) \cdot Fe(SO_4)_2 \cdot (H_2O)_2$ and 10 % of szomolnokite $(Fe(SO_4) \cdot H_2O)$. Presumably, undetermined fluorine may be related to the solid phase formed resulting from distillation.

Energy costs

Approximately 70.2 kg of HF equivalent to the content of 175.5 kg of 40 % HF passes to the distillate in the processing of 1 m³ of process acid fluoride-sulphate solution, taking into account the initial concentration of HF in the process solution of 78 g/L, and distillation degree of 90 %. Additionally, H_2SO_4 is regenerated and lime content for neutralization is excluded. Herewith, energy costs for processing of 1 m³ of the solution (when heated to 140 °C) do not exceed 4500 RUB.

The high solubility of lanthanide fluorides compared to their dissolution in monobasic acids observed in [15, 16] may be explained using the findings. Our earlier [17] observations of a decrease in concentration of fluorine determinable by potentiometric titration relatively to its introduced amount in pH correction with sulphuric acid, which was not found in case of nitric or hydrochloric acids are also explained.

CONCLUSION

It has been shown that significant amounts of fluorosulphonic acids are formed in solutions containing hydrofluoric and sulphuric acids. Herewith, with increasing concentrations of acids, their interaction degree with the formation of HSO_3F rises. An increase in mixture heating temperature leads to a significant rise in acidity, which is directly related to a decrease in the content of HSO_3F . The larger concentrations of acids (especially sulphuric) are, the higher heating temperatures are required to decompose HSO_3F .

An opportunity for HF direct distillation

from process fluoride-sulphate solutions at 170–190 °C has been demonstrated. Herewith, distillate (HF solution) contains no more than 0.54 % of H₂SO₄, and the residue of sulphuric acid solution – less than 1 % of HF.

HF distillation temperature decrease does not bring about satisfactory results.

Increasing the temperature to 200–250 °C increases the intensity of distillation of hydrogen fluoride with a minor rise in the content of H₂SO₄ in the exhaust gases.

REFERENCE

- Goroshhenko Ya. G. Fiziko-khimicheskie issledovaniya pererabotki redkozemelnyh titanoniobatov sernokislotnym metodom. M.–L.: Izd-vo AN SSSR, 1960. 183 p.
- Majorov V. G., Nikolaev A. I., Kopkov V. K., Elizarova I. R., *Khim. tekhnologiya*. Vol. 16, No. 1. 2015. P. 32–45.
- Smirnov A. V., Nechaev A. V., Koznov A. V., Sokolov V. D., Aktualnye voprosy polucheniya i primeneniya RZM-2015: Sb. mater. mezhdunar. nauch.-prakt. konf. M.: OAO "Institut GINTsVETMET", 2015. P. 36–39.
- Baklanova I. V., Majorov V. G., Kopkov V. K., Balczat V. I., Mimonov A. V., Nikolaev A. I., *Khim. tekhnologiya*. 2001. No. 2. P. 28–32.
- Khimicheskaya produkcija – ZAO "SP KhIMPROM". [Elektronnyj resurs]: UEL:<http://khimprom-s.ru/h2so4.phtml> (accessed 03.09.2017)
- Petrov V. B., Muzhdabaeva M. A., Prokof'eva T. A., Fiziko-khimicheskie i tekhnologicheskie issledovaniya pererabotki mineralnogo syrja. Apatity: KNTs RAN, 1989. P. 84–87.
- Tananaev I. V., *ZhPKh*. 1932. Vol. 5, No. 6–7. P. 834–842.
- Ryss I. G. Khimiya ftora i ego neorganicheskikh soedinenij. M.: Gos. nauch.-tekhn. Izd-vo khim. literatury, 1956. 718 p.
- Lange W., *Zeitschrift fur anorganische und allgemeine Chemie*. 1993. Vol. 215, Issue 3–4. P. 321–332.
- Ostrovskij S. V., Amirova S. A., *ZhPKh*. 1969. Vol. XLII, No. 11. P. 2405–2409.
- Polyakova E. M., Zelenskaya A. I., Tr. UNIKHIM "Rabotyv oblasti tekhnologii solej i sernoj kisloty. 1954. No. 1. P. 64–67.
- Ostrovskij S. V., Nazarov S. A., Kurkanin V. N., Ostrovskaya T. V., Issledovaniya v oblasti khimicheskij tekhnologii. Sb. tr. Perm. politehn. In-ta. Perm, 1974. P. 100–104.
- Pat. 2147621 RF, MPK7 S22V34/24, 59/00, 34/12, 3/06, S01P23/04 RF, 2000.
- Vasil'ev B. T., Otvagina M. I. Tekhnologiya sernoj kisloty. M.: Khimiya, 1985. 384 p.
- Lokshin E. P., Vershkova Yu. A., Ivlev K. G., Tareeva O. A., *ZhNX*. 2004. Vol. 49, No. 4. P. 707–710.
- Lokshin E. P., Tareeva O. A., *ZhPKh*. 2007. Vol. 52, No. 12. P. 1–5.
- Lokshin E. P., Belikov M. L., *ZhPKh*. 2008. Vol. 81, No. 2. P. 177–181.