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Separation and recovery of NaF from fluorine containing solution by the common ion effect of Na^{+}

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Abstract

The separation and recovery of NaF from fluorine containing solution by the common ion effect of Na^{+} was studied. The solubility of NaF in the solutions of NaCl, NaNO$_3$, Na$_2$CO$_3$, Na$_2$SO$_4$ and NaOH at 30 °C was determined. It was found that when the compound containing sodium, such as Na$_2$CO$_3$ or Na$_2$SO$_4$ was added into NaF saturated solution to product the common ion effect of Na^{+}, most of the NaF can be crystallized without evaporating concentration, and the added Na$_2$CO$_3$ or Na$_2$SO$_4$ can be recovered by cooling crystallization. Combining cooling crystallization with the common ion effect of Na^{+}, different processes can be designed to recover NaF from different fluorine containing solutions. This will have a significant impact on the treatment of fluorine containing wastewater and the recycling of fluorine resources.

Keyword: Analytical chemistry

1. Introduction

Sodium fluoride (NaF), one of the most frequently used fluoride compound is composed of Na^{+} and F^{-} [1]. The solubility of NaF is about 42 g/L (1 mol/L) at room temperature, and it increases very slowly with the increase in temperature

[2]. Therefore, apart from the neutralization of HF with Na_2CO_3 or NaOH, other processes of NaF production all require evaporation and crystallization [3].

With the development of modern industry, the use of fluorine-containing compounds is increasing [4]. The increase in the use of fluorine-containing compounds will inevitably lead to an increase in fluorine containing wastewater. The treatment of fluorine containing wastewater has become an important issue in the field of environmental protection [5, 6]. Many methods have been developed to purify fluorine containing wastewater, such as chemical precipitation, coagulation precipitation, adsorption, ion exchange and so on [7, 8, 9, 10, 11, 12]. After fluorine containing wastewater is converted into fluorine containing solid waste, such as mixture of CaF_2 and $CaSO_4 \cdot 2H_2O$ or CaF_2, $CaSO_4 \cdot 2H_2O$ and $Al_2O_3 \cdot xH_2O$, it is easy to cause secondary pollution. With adsorption or ion exchange, fluorine can be separated and enriched, but the concentration of F in feed solution is limited under normal conditions [13], and it is not economical to recover sodium fluoride from the desorption solution by evaporation concentration.

Recently, we have found that using the common ion effect of Na^+, NaF can be directly separated and recovered from fluorine containing solution without evaporating concentration. Thus the objectives of this study are (i) to determine the solubility of NaF in sodium containing solutions and (ii) using the common ion effect of Na^+ to separate and recover NaF from the solution containing F^- without evaporation concentration.

2. Experimental

2.1. Materials and analysis

The titanium processing washing wastewater was provided by Baoji Titanium Industry Co., Ltd., Shanxi province, China. The zinc sulfate solution was supplied by Danxia smelter, Guangdong province, China. The chemical reagents NaF, $NaNO_3$, NaCl, Na_2CO_3, Na_2SO_4 and NaOH were used in the experiments, which are all analytical grade.

Fluorine was determined using a fluoride ion selective electrode (PF-1, Kangyi instrument Ltd., China). The contents of other elements were determined by inductively coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The pH was determined with ORION-230A which was made in USA; the degree of accuracy is 0.01.

2.2. NaF separation procedure

In order to use the common ion effect of Na^+ to separate and recover NaF from fluorine containing solution, the solubility of NaF in the solutions containing sodium

was determined. After the fluorine containing solution was turned into sodium fluoride solution, compounds containing sodium were added into to produce the common ion effect of Na^+ to force NaF crystallized. At last, the added compounds were recovered by cooling crystallization for reuse.

3. Results and discussion

3.1. Solubility of NaF in the solutions containing sodium

The solubility of NaF in the solutions containing sodium is shown in Fig. 1, curve 6 is the theoretical value at 30 °C ($Ksp_{(NaF)} = 1$) [2], the other curves were obtained by adding $NaNO_3$, NaCl, Na_2CO_3, Na_2SO_4 and NaOH into NaF saturated solution respectively at 30 °C stirring for 12 h, and then determining the concentrations of F^- and Na^+ in the solution after filtration. As can be seen, the solubility of NaF in the solutions containing sodium is affected by the common ion effect of Na^+, and the solubility of NaF in the solution of $NaNO_3$ is almost as the theoretical value; the solubility of NaF in the solution of Na_2CO_3 is greater than the theoretical value until Na_2CO_3 is saturation; the solubility of NaF in the solution of NaCl or NaOH is less than the theoretical value; while the solubility of NaF in the solution of Na_2SO_4 is more complex, it is greater than the theoretical value when the concentration of Na^+ is ≤ 47.75 g/L, then it is less than the theoretical value with the further increase in Na^+ concentration until Na_2SO_4 is saturation.
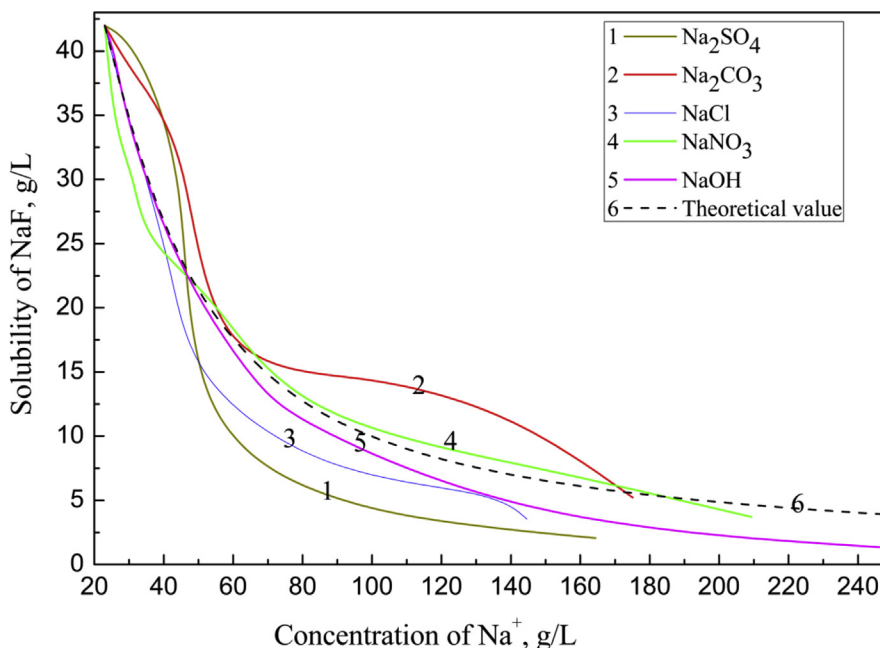

Fig. 1. Solubility of NaF in the solutions containing sodium at 30 °C.

It was found that before these sodium salts except Na_2SO_4 reach saturation, NaF cannot co-crystallize with them. This is due to that the solubility of NaF is much less than the solubilities of $NaNO_3$, Na_2CO_3 and NaCl [2], which facilitates the separation and recovery of NaF from their solutions.

3.2. Reutilization of compounds containing sodium

The solubility curves of $NaNO_3$, Na_2CO_3, Na_2SO_4 and NaCl in aqueous solution are shown in Fig. 2, which is drawn with the solubility data of $NaNO_3$, Na_2CO_3, Na_2SO_4 and NaCl [2]. As seen, the solubility of $NaNO_3$ in water is very high, and its solubility increases rapidly with the increase in temperature, even at 0 °C, its solubility is more than 730 g/L; the solubility of NaCl increases very slowly with the increase in temperature; while the solubilities of Na_2CO_3 and Na_2SO_4 are more complex, they are both increase significantly with the increase in temperature when temperature is ≤40 °C, and then they decrease slowly with the further increase in temperature. With the decrease in temperature from 40 °C to 0 °C, the solubility of Na_2CO_3 decreases from 490 g/L to 70 g/L, and that of Na_2SO_4 decreases from 490 g/L to 49 g/L. This indicates that by adding Na_2CO_3 or Na_2SO_4 into fluorine containing solution to produce the common ion effect of Na^+, not only can NaF be crystallized, but also the added Na_2CO_3 or Na_2SO_4 can be recovered by cooling crystallization. Therefore, Na_2CO_3 or Na_2SO_4 can be reutilized in the separation and recovery of NaF from the solution containing fluorine without evaporating concentration.
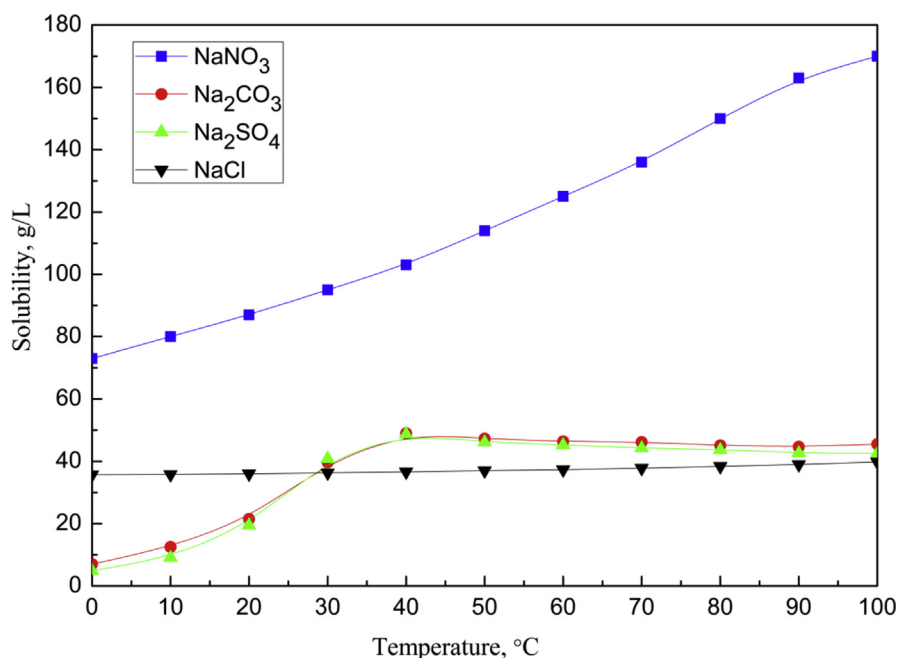

Fig. 2. Solubility curves of sodium salts.

3.3. Separation and recovery of NaF

It is well known that the fluorine ion (F⁻) in fluorine containing solution can be absorbed by adsorbent, and the loaded adsorbent can be desorbed and regenerated with Na_2CO_3 or NaOH solution [14, 15]. Utilizing the solubility characteristics of Na_2CO_3 and the common ion effect of Na^+, the fluorine in zinc sulfate solution can be separated and recovered using the flowsheet as shown in Fig. 3. The zinc sulfate solution used in the experiment contains Zn 115−125 g/L and F 216 mg/L. When the solution pH was adjusted to 4.5−5.1, the powder of $Ce_2(CO_3)_3 \cdot 8H_2O$ was used as the adsorbent to remove F to <50 mg/L. Then the load adsorbent was regenerated in 2 mol/L Na_2CO_3 solution. It was found that the F in the desorbed solution can be precipitated in the form of NaF by adding Na_2CO_3 to increase the concentration of Na^+ to above 75 g/L. After filtration, the qualified product of NaF was obtained by washing the NaF cake with NaF saturated solution. Then the solid of sodium carbonate was separated and recovered from the precipitated solution by cooling crystallization at 0−5 °C. The crystallized solution can be returned to the desorption process, and the crystals of sodium carbonate can be reused as promoters to force the precipitation of NaF from the desorbed solution. Thus the product of NaF can be obtained from the desorption solution without evaporation. The adsorption and de-adsorption of fluorine can be expressed by the following equations [16]:
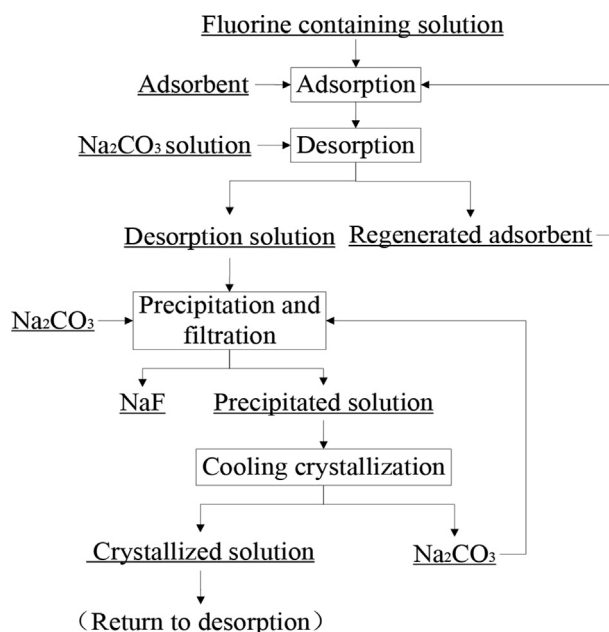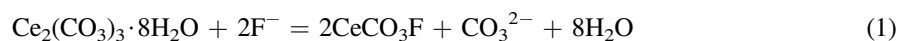
$$Ce_2(CO_3)_3 \cdot 8H_2O + 2F^- = 2CeCO_3F + CO_3^{2-} + 8H_2O \tag{1}$$

$$2CeCO_3F + Na_2CO_3 + 8H_2O = Ce_2(CO_3)_3 \cdot 8H_2O + 2NaF \tag{2}$$

Fig. 3. Flowsheet of NaF production with fluorine containing solution by adsorption.

In a similar way, NaF can be obtained from different fluorine containing solutions. For example, NaF was obtained from the titanium processing washing wastewater. The wastewater contains 20−30 g/L HNO_3, 3−8 g/L F and some titanium ions. When the wastewater is neutralized with NaOH and/or Na_2CO_3, it will be turned into the NaF solution containing $NaNO_3$. From Fig. 1 it can be found that the solubility of NaF decreases with the increase in Na^+ concentration in the solution. After filtration, adding H_2SO_4 into the filtrate to turn the $NaNO_3$ into the crystal of sodium sulfate by cooling at −10 ∼ −15 °C, so the HNO_3 solution containing a few HF was obtained, which can be used to prepare the washing solution of HNO_3-HF.

4. Conclusion

Experiments indicate that by adding a compound containing sodium to produce the common ion effect of Na^+, the crystal of NaF can be obtained from fluorine containing solution without evaporating concentration, and if the added compound is Na_2CO_3 or Na_2SO_4, it can be recovered by cooling crystallization. Therefore, combination the common ion effect of Na^+ with the methods removing fluorine from fluorine containing solution, the product of NaF can be obtained from it.

Declarations

Author contribution statement

Xue-Wen Wang, QiGe: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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