

## Conference Paper

# Sorption Removal of Fluorine Ions, Incoming with the Recycling Zinc-Bearing Materials

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### Abstract

The possibility of using inorganic sorbent, iron oxyhydrate (IOH) to remove  $F^-$  ions from technological solutions of zinc production is considered in this article. The principal possibility of the use of ion-exchange resins as carriers modified by IOH is considered. The formation of the active substance on cation-exchange resins was studied. It was shown that the most durable composite sorbents were obtained using strong-acid cation-exchange resins with  $SO_3^-$  groups. A method for introducing IOH into the structure of carrier materials and obtaining composite sorbents is described. The strong acid cation exchanger KU-2x8 is recommended as the basis of the composite.

**Keywords:** iron oxyhydrate, ion exchanger, sorption, fluoride ion, purification

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## 1. Introduction

It is of current interest the challenge of removal of ultralow concentration of impurities in solutions of metallurgical, chemical, petrochemical and metalworking enterprises. This is concern both for wastewaters purification and for solution treatment operations.

Environmental and resource-efficient technologies encouraging legislative initiatives oblige the companies to introduce technologies that have no effect on the profit directly. However, the world's commodity market prevent companies (zinc producers) to include additional costs and force it to decrease costs of zinc by increasing the production. At the same time zinc raw materials base is substantially limited. All the foregoing begs the question of involving the anthropogenic and secondary zinc raw materials in treatment jointly with metallic minerals.

Electric arc furnaces' dusts (EAFD) is one of the most promising raw material for zinc production [1, 2]. In zinc production the Waelz process for EAFD treatment is widespread. These materials can be refined in rotary furnaces (Waelz process) to separate the zinc from other elements. Resulting product has high level of zinc and it is convenient for further processing. However, beyond the zinc, cadmium and lead the halides are evaporated to fume significantly.

The  $F^-$  and  $Cl^-$  ions containing in the electrolyte enhance the corrosion of cathodic zinc [3]. Extremely negative influence is exerted by the excess content of fluorine, which is manifested in the effect of "difficult stripping". At the same time, it becomes impossible to use automated cathode-stripping lines, but manual stripping has low efficiency and is associated with significant costs. In addition to the trouble of the operating mode of the electrolysis shop, a part of the cathode zinc that cannot be separated from the aluminum matrix is subjected to dissolution and redirected to electro winning.

The average concentration of chlorine in the productive zinc solution during processing of raw materials is 20-300 mg/dm<sup>3</sup>, fluorine is 20-50 mg/dm<sup>3</sup>. However, at the recycled secondary raw materials is involved, the halide content in the solution can be significantly increased. And if the technology of chlorine removal in the form of monovalent copper compounds is successfully used in the practice of enterprises, the experience of zinc solutions purification from fluoride at operating conditions is absent at present. Thus, the choosing of the optimal technology of purification of zinc sulfate solutions from fluorine is urgent.

Part of the fluorine is removed in the form of calcium fluoride at the stage of neutral leaching. However, the solubility of this compound is about 20 mg/dm<sup>3</sup> for pure solutions and is substantially increased in the presence of manganese, whereby the fluorine content is significantly higher than the value providing an automated cathode deposit stripping. One of the effective methods provides decreasing of fluorine content to acceptable value is sorption. Sorption purification from fluorine is possible either by anion exchange resins [4] or inorganic substances - activated alumina [5], iron oxyhydrates [6] and composite sorbents [7]. There is number of research that describe methods of synthesis of nanocrystalline sorbents usable for fluoride removal. However, the use of the ultrafine particles for treating of zinc electrolytes is complicated owing to pulp separation. This effect could be eliminated by putting the particles of IOH on the carrier. Such composite sorbents on the base of cation exchange resin with compounds of iron, embedded into polymer matrix can be applied for removal of cations and anions in the wide range of pH [8, 9]. Thus, new composite sorbent, using cation exchange resin as a carrier and iron oxyhydrates as an active species were chosen for fluoride removal.

## 2. Experimental

Cation exchange resin was used as a basis for new composite sorbent synthesis. For this purpose, the resin was saturated by ferric ions and conditions of synthesis of iron oxyhydrates were provided. Cation exchange resins KU-2×8 and KU-23 are copolymers

Species	Concentration 1		Concentration 2	
	C <sub>1</sub> (Fe), g/dm <sup>3</sup>	pH <sub>1</sub>	C <sub>2</sub> (Fe), g/dm <sup>3</sup>	pH <sub>2</sub>
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ×9H <sub>2</sub> O	0,13	2,8	0,95	1,95
FeSO <sub>4</sub> ×7H <sub>2</sub> O	0,36	4,47	1,77	3,75
FeCl <sub>3</sub>	0,11	3,75	1,16	2,1

TABLE 1: Conditions of resin saturation by ferric ions.

of styrene and divinylbenzene with -SO<sub>3</sub>H functional groups. KU-2×8 has gel structure and KU-23 has macroporous one.

To assess the impact of ferric content in resin on the fluoride exchange capacity series of tests were carried out. For saturation of resin by ferric ions solutions of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeSO<sub>4</sub>, FeCl<sub>3</sub> were used. Conditions of ferric ion sorption described in Table 1.

The modification method involving the use of an iron (II) salt solution was used to provide an optimum pH value at which the cation exchange capacity for iron is maximized.

In the case of use of ferrous sulfate, it was additionally oxidized to Fe<sup>3+</sup> by hydrogen peroxide. Then, the formation of iron oxyhydrate was carried out in the ionite phase according to the procedure described above.

The fluoride sorption was carried out in static mode during 24 hours. The model solution with fluoride concentration 100 mg/dm<sup>3</sup> and pH 5.5 was used. After sorption the sorbent was separated from solution and washed by distilled water and stripped by alkali solution with concentration of 0.1 M. Fluoride concentration in eluates were determined by ion-specific electrode potentiometry. Results are shown in Figure 1.

It has been shown that the higher ferric content in resin correspond to the higher fluoride exchange capacity. Also it is noted that KU-2×8 has higher ferric exchange capacity than KU-23.

Method of resin modification using ferrous ions with its subsequent oxidation does not provide any advantage in ferric level.

On the other hand, with a comparable iron content in the sorbent, the capacity for fluoride is lower than when using ferric iron. This can be explained by the incomplete oxidation of ferrous ions in the phase of resin.

When FeCl<sub>3</sub> is used as iron source the values of fluorine capacity are somewhat higher when using Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. However, the use of ferric chloride is complicated by the high hygroscopicity of the reagent and its corrosive activity.

Composite sorbents are obtained on the base of ion exchange resins has been loaded in the ferric salts solutions show stability in the wide range of pH (from 1 to 12).

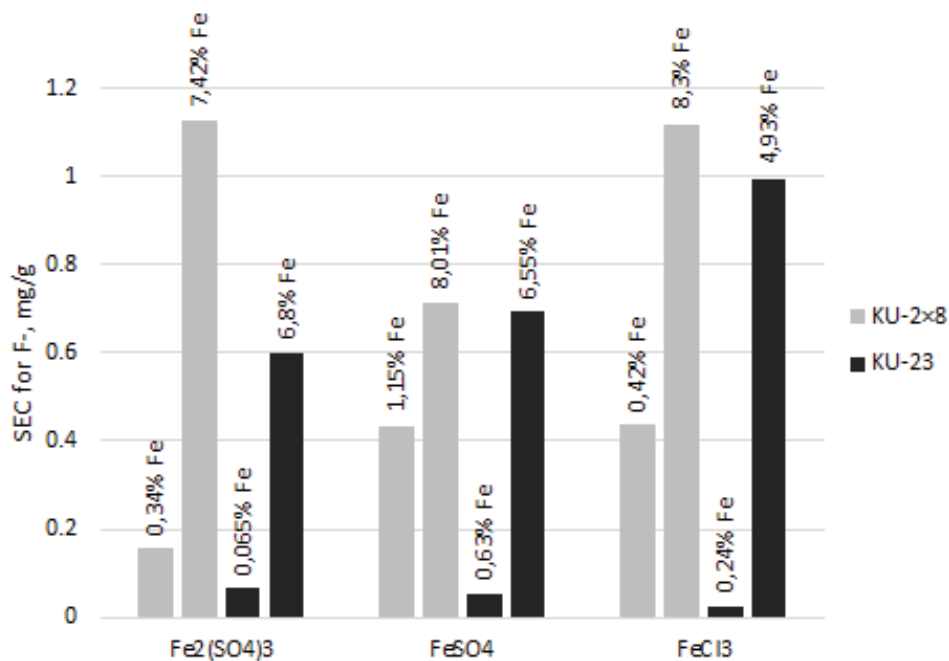


Figure 1: Effect of the ferric content in resin on fluoride exchange capacity.

Sample	Index	Cycle 1	Cycle 2	Cycle 3
KU 2x8 N <sup>o</sup> 1	SEC, [mg/g]	0,74	0,72	0,68
	Absorbtion rate, [%]	37,01	35,04	34,03
	Stripping rate, [%]	89,13	87,78	93,61
KU 2x8 N <sup>o</sup> 2	SEC, [mg/g]	1,17	1,03	0,99
	Absorbtion rate, [%]	29,25	25,75	24,75
	Stripping rate, [%]	84,82	79,52	88,63

TABLE 2: Cyclic test of the composite sorbent.

To explore the new composite sorbent characteristics during operation number of sorption/stripping cycles were conducted. In tests composite based on KU-2x8 was used. Sample of resin was saturated by ferric ions in the solution of ferric sulphate with C(Fe<sup>3+</sup>) - 0.1M. Ferric containing cation exchange resin washed by deionized water and was contacted with sodium chloride solution (0.05 M) for 24 hours. The sorbent was dried at 25 °C. The samples of resin were placed in sodium fluoride solution with concentration 50 mg/dm<sup>3</sup> of fluoride (for sample 1) and 100 mg/dm<sup>3</sup> (for sample 2) for 24 hours. After that the sorbent was separated from solution and stripped by alkali solution with concentration of 0.1 M. Sorption/stripping cycles were repeated. Fluoride concentration in filtrates and eluates were determined by ion-specific electrode potentiometry. Results are shown in Table 2.

### 3. Conclusions

The problem of removal of fluoride ions from zinc-containing solutions was studied, using iron oxyhydrate as active substance. A method of producing a composite sorbent it is proposed.

Previous experiments of formation of iron oxyhydrates coatings on anion exchange resins has been shown that iron compounds do not have a stable bond with anionite grains and are exfoliated during operation. On the contrary cationite forms a strong bond with iron by functional groups. Iron compounds can be removed only by treatment in solutions with high acidity or in presence of strong complexing agents. It was found that an increase in the iron content in modified cation exchangers over 5% does not lead to a significant increasing of the capacity of the sorbent for the fluoride ion. At the same time, the presence of free functional groups of ion exchanger provides the possibility of additional purification of solutions from metal ions.

It is recommended to use strongly acid cationite KU-2x8 as a carrier. The capacity of obtained sorbent for fluoride is 1.1 mg/g, the drop in capacity after 3 cycles of sorption is 10-15%. Desorption is recommended to be carried out by solutions of NaOH with a concentration of 4 g/dm<sup>3</sup>, Desorption rate is 80-95%.

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