



IMPROVING THE EFFICIENCY OF PURIFICATION IN THE TECHNOLOGICAL CYCLES OF LIMESTONE PROCESSING

Smirnova Ekaterina and Denis Lutskiy

Department of Physical Chemistry, Saint Petersburg Mining University, Russian Federation, Saint-Petersburg, line, Russia

E-Mail: smiree@mail.ru

ABSTRACT

In the article, from the standpoint of an integrated systems approach, a theoretical rationale is presented for the choice of an efficient method for the removal of fluorine from wastewater from industrial enterprises engaged in the processing of limestone.

Keywords: limestone, separation, purification, fluoride, phosphorus, calcite, dolomite, magnesite, siderite.

INTRODUCTION

The production activity of mankind is associated with the use of a variety of natural resources, covering most of the chemical elements. A particularly important biogeochemical cycle, determining the existence of man on Earth, has a water cycle in the biosphere. If we take into account the fact that almost all inorganic compounds, and partially organic compounds, dissolve in water, we can understand the main role of water in the transfer and distribution of chemical elements between hydro, litho and atmosphere, since water can simultaneously exist in three states of aggregation (liquid, gaseous and solid).

The mining and chemical industries in Russia, which process phosphate rock and produce phosphoric acid and phosphate mineral fertilizers (double superphosphate, ammophos), have a negative impact on the geo-ecological circulation of phosphorus and fluorine.

The geoecological circulation of phosphorus and fluorine takes place in the system "natural mineral $[\text{Ca}_{10}(\text{PO}_4)\text{CaF}_2]$ → sulfuric acid industrial processing → mineral fertilizers → soil → plants → animals → soil → aquatic environment". The main environmental hazards are phosphorus and fluorine, which are in the produced phosphoric acid, and toxic production wastes, which are stored in sludge dumps and pollute the environment. In accordance with this, the development of theoretical foundations, scientific statements and technological solutions to eliminate the negative impact of fluorine and phosphorus on the environment is relevant.

LITERATURE REVIEW

Large-tonnage waste from the production of phosphate fertilizers is phosphogypsum, which is obtained by processing apatite concentrate of 4.25 tons, and during processing of phosphate rock - 5.6 tons per ton of extraction phosphoric acid (Lutskiy et al 2018). A large amount of waste occurs during work related to the development of phosphate mineral deposits. Their number often exceeds the amount of extractable concentrate. The subsequent processing of phosphate concentrate is also associated with the formation of large volumes of waste, since the existing technological schemes are developed, as a rule, in order to extract the main component of

phosphoric acid from the raw material. As a result, waste dumps of "empty" rock grow in the areas of mining, enrichment and processing of mineral raw materials, which are a source of pollution of surface and groundwater. A significant proportion of waste enters the atmosphere and into water bodies with wastewater (Gordashevsky *et al.* 1987).

Production activities of LLC PG Phosphorit in the territory of the Kingisepp District of the Leningrad Region, located on the coast of the Gulf of Finland, led to the accumulation of a significant amount of industrial waste in the form of:

- quartzite - phosphorite enrichment products;
- phosphogypsum - products for phosphoric acid;
- phosphate minerals - products of enrichment of natural phosphorites.

Systems analysis leads to the conclusion that the natural resources themselves form the pollution of the biosphere. Huge funds, energy, time are spent on their mining, processing, transportation, but ultimately, the quality of the environment deteriorates. Man-made systems "resources - production - consumption - resources" cannot be called cycles, by analogy with natural biogeochemical systems, since there is no clear relationship between the final stages of consumption and the initial stages of extraction and preparation of natural resources. These artificial systems in modern chemical production are part of large-scale natural resource cycles of the biosphere.

Fluorine trapping from industrial waste gases has been established in many superphosphate plants. Methods of co-production of fluoroproducts in the production of simple and double superphosphates, extraction phosphoric acid and desfluorinated phosphates have been developed and partially mastered. However, at the same time only 25-28% of fluorine contained in the initial phosphate raw material is utilized. Part of the fluoride enters the fertilizer, solid waste and wastewater, which raises problems related to environmental protection.



The properties of fluorine to be a universal ligand determine a wide range of geochemical conditions of its transition into water during interactions in the "water - crystal" system. From the analysis of the solubility diagrams of sodium fluoride and calcium in water, depending on temperature, it follows that the compounds of calcium salts of fluorine are distinguished by a very low solubility, CaF_2 ($\text{SP}(\text{CaF}_2)$ is 10^{-11}). Due to the high solubility of NaF crystal (at 20 °C, 4.3 wt.%), Wastewater and groundwater are always under saturated with fluorine, and they are capable of dissolving NaF, accumulating it and increasing the degree of mineralization of these waters, which leads to an increase in their contents fluoride ions.

Due to the different solubility of sodium and calcium fluorides, the transfer of fluorine from rocks to groundwater, as well as its content in these waters, depends on the ratio of $\text{Na}^+/\text{Ca}^{2+}$ ions in them, and the greater this ratio in groundwater and wastewater, the more fluoride other things being equal, they may be contained.

Therefore, the fluorine content in groundwater and wastewater is limited by the content of calcium ions.

In this regard, in the presence of the elements of complexing agents Be, Mg, Ca, which form stable complex compounds with fluorine, the solubility of fluorine-containing compounds increases.

Fluorocomplex compounds decompose only in alkaline media (equation 1) and, therefore, fluorocomplex compounds with the Be, Mg, Ca cations of groundwater are widespread in acidic and neutral waters. In this case, the more stable the complex compound, the more intense the fluorine passes into the aqueous phase.

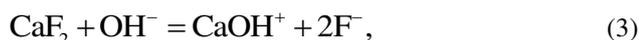


Table-1 presents data that show that fluorine is a universal complexing agent and therefore fluorocomplex compounds of the elements Be, Mg, Ca have a relatively high stability, since the values of the logarithm of the stability of the constants of complex compounds have positive values.

Table-1. The degree of stability of fluorocomplexes.

Elements	Degree of complexation				
	1	2	3	4	5
Be^{2+}	5,88	10,8	14,4	16,4	
Mg^{2+}	1,8				
Ca^{2+}	1,1				
Al^{3+}	6,13	11,15	15	17,75	19,4
Fe^{3+}	5,28	9,3	12	14	14,42

At the same time, the toxic element beryllium has the greatest stability in aqueous solutions. Therefore, the solubility of fluorite (calcium fluoride CaF_2) increases in the presence of hydrogen and hydroxyl ions (equation 2, 3).



Thus, groundwater containing ions Na^+ , HCO_3^- is always more favorable for the extraction of fluorine from rocks and its accumulation due to the equation 3. Therefore, the content of fluorine in groundwater and wastewater is usually increased and the hydrothermal solution, being in constant contact with the rocks of the earth's crust, cannot have an arbitrary composition - it is governed by the water-rock interaction.

RESULTS AND DISCUSSION

The specificity of the hydrothermal process is that it provides mobilization, transportation and concentration of the scattered elements of the earth's crust,

including ore ones. The behavior of ore elements at all stages of the development of hydrothermal systems is subject to the interaction of "water-rock" in its various manifestations.

The residual concentration of the harmful fluorine in water is determined from the molar solubility of hardly soluble compounds, the values of which are given in Table-2.

Table-2 also presents chemical reactions, on the basis of which fluorine can be removed from wastewater and the values of the equilibrium fluorine content.

The physicochemical properties and thermodynamic characteristics of fluorine determine the geochemical conditions of its transition into water during interactions in the "water - natural crystal" system. The intensity of dissolution of crystalline fluorine compounds is determined by the rule of like ions and the ionic strength of the solution.

The solubility of complex fluorine-containing compounds is also a function of complexation in aqueous solutions. Therefore, in the presence of complexing elements forming stable complex compounds with fluorine, the solubility of fluorine-containing compounds increases.

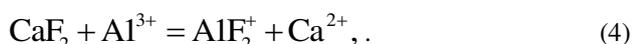


In this case, the more stable the complex aqueous phase. compound, the more intense the fluorine passes into the

Table-2. The results of the calculation of the molar solubility of various compounds containing fluorine.

No	Solubility in water	$\Delta G = \eta E_{\min}$, kJ / mol	Literary	Calculated	S, mol/dm ³
			-lg (SP)		
1	$\text{NaF} \Leftrightarrow \text{Na}^+ + \text{F}^-$	4,3	0,49	0,75	$4,2 \cdot 10^{-1}$
2	$\text{KF} \Leftrightarrow \text{K}^+ + \text{F}^-$	-23,7	-	-4,15	-
3	$\text{MgF}_2 \Leftrightarrow \text{Mg}^{2+} + 2\text{F}^-$	55,9	9,79	9,78	$1,32 \cdot 10^{-2}$
4	$\text{CaF}_2 \Leftrightarrow \text{Ca}^{2+} + 2\text{F}^-$	63,3	11,09	11,07	$1,27 \cdot 10^{-3}$
5	$\text{AlF}_3 \Leftrightarrow \text{Al}^{3+} + 3\text{F}^-$	99,2	17,78	17,37	$1,14 \cdot 10^{-5}$
6	$\text{FeF}_3 \Leftrightarrow \text{Fe}^{3+} + 3\text{F}^-$	114,5	20,0	20,07	$1,09 \cdot 10^{-2}$
7	$\text{Na}_3\text{AlF}_6 \Leftrightarrow 2\text{Na}^+ + \text{Al}^{3+} + 6\text{F}^-$	194,4	-	34,07	$1,09 \cdot 10^{-2}$
8	$\text{Na}_3\text{AlF}_6 \Leftrightarrow 3\text{Na}^+ + \text{AlF}_6^{3-}$	75,2	-	13,18	$2,22 \cdot 10^{-2}$
9	$\text{Na}_2\text{SiF}_6 \Leftrightarrow 2\text{Na}^+ + \text{SiF}_6^{2-}$	25,8	-	4,51	$1,97 \cdot 10^{-2}$
10	$\text{K}_2\text{SiF}_6 \Leftrightarrow 2\text{K}^+ + \text{SiF}_6^{2-}$	37,6	7,09	6,58	$5,04 \cdot 10^{-2}$
11	$\text{CaSiF}_6 \cdot 2\text{H}_2\text{O} \Leftrightarrow \text{Ca}^{2+} + 4\text{HF} + \text{H}_4\text{SiO}_4$	12,7	-	2,31	0,16

The solubility of fluorite (calcium fluoride CaF_2) increases not only in the presence of hydrogen (equation 2) and hydroxyl ions; (equation 3), but also in the presence of aluminum in acidic media (equation 4):



The main difference of fluorine from other halogens is the low solubility of calcium salts in water, which increases in the series $\text{CaF}_2 \rightarrow \text{CaCl}_2 \rightarrow \text{CaBr}_2 \rightarrow \text{CaI}_2$.

Below are the chemical reactions of defluorization of solutions based on the use of carbonate, oxide and calcium hydroxide.

Table-3. The Gibbs free energy of various defluorization chemical reactions.

Chemical reactions	Gibbs free energy, kJ/mol
$\text{CaCO}_3 + \text{HF} = \text{CaF}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$	- 121,3
$\text{Ca}(\text{OH})_2 + 2\text{HF} = \text{CaF}_2 + 2\text{H}_2\text{O}$	- 156,8
$\text{CaO} + 2\text{HF} = \text{CaF}_2 + \text{H}_2\text{O}$	- 213,2

The sequence of recording chemical reactions corresponds to the various technological stages of the preparation of calcium hydroxide reagent: natural limestone \rightarrow roasting calcium oxide (CaO) \rightarrow calcium hydroxide $\text{Ca}(\text{OH})_2$. The results of the Gibbs energy calculation of the defluorization reactions show that fluorine can be removed from solutions using all of the above compounds, with the use of calcium oxide being the most effective. Natural calcium carbonates (limestones), in addition to the main component of calcium, contain

magnesium, silicon, iron, aluminum and other elements. In connection with the above, it is desirable to synthesize inorganic reagents of a given composition, which can be obtained by thermal calcination of limestone, for the treatment of wastewater from fluorine (Sizyakov *et al.*, 2017, Sizyakov *et al.*, 2018, Brichkin *et al.*, 2016).

Below are the calculated values of the chemical potentials of carbonate, oxide and hydroxide of calcium, magnesium, iron, used in the process of removing fluoride from solution.



Table-4. The values of the chemical potentials of carbonate, oxide and hydroxide of calcium, magnesium, iron, used in the process of removing fluoride from solution.

Compound	η, J	Compound	η, J	Compound	η, J
Calcite $CaCO_3$	4,67	Calcium hydroxide	4,45	Calcium oxide	3,59
Dolomite $CaMg[CO_3]_2$	4,78	Calcium hydroxide and magnesium	4,55	Calcium and magnesium oxides	3,8
Magnesite $MgCO_3$	4,88	Magnesium hydroxide	4,65	Magnesium oxide	4,01
Siderite $FeCO_3$	5,34	Iron hydroxide	5,15	Iron oxide	4,93

The temperature of reducing thermal decomposition of natural carbonate minerals can be arranged in the following sequence:



Thus, knowing the magnitude of the chemical potential, it is possible to adjust the composition of the initial limestone and predict the technological conditions for the creation of new de-fluorinating chemicals (Alekseev *et al* 2004).

CONCLUSIONS

The performed theoretical calculations show that the final composition of the process reagent (the required composition of lime) can be obtained by changing the natural limestone by introducing the specified inorganic additives into the crystal structure. The mineralogical analysis of lime, carried out after calcining limestone, shows that the introduction of calcium and magnesium silicate impurities into the lime structure, as well as Na_2O , MgO , Fe_2O_3 impurities, increases the activity of the final product in the mixture, as evidenced by an increase in its potential from 3.59 to 4.27 eV.

The calculated values of the chemical potential show that all the considered complex inorganic reagents $x(Ca, Mg)O \cdot ySiO_2$, $x(Ca, Mg)O \cdot y(Al, Fe)_2O_3$ can be used to remove fluoride from the solution, however, the greatest chemical calcium aluminates have activity, and the higher the molar ratio CaO/Al_2O_3 , the higher their activity with respect to fluorine (Lyubovina *et al* 2018).

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