

Hydrolysis of iron and chromium fluorides: Mechanism and kinetics

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Abstract

Fluoride complexes of metallic ions are one of the main problems when processing industrial effluents with high content of fluoride anion. The most important case is derived from pickling treatment of stainless steel, which is performed with HNO₃/HF mixtures to remove oxides scale formed over the metal surface. Waste from this process, spent pickling liquor, must be treated for recovering metallic and acid content. Conventional treatments produce a final effluent with high quantity of fluoride complexes of iron and chromium. This work proposes a hydrolysis treatment of these solid metal fluorides by reacting them with a basic agent. Metal oxides are obtained, while fluoride is released to solution as a solved salt, which can be easily recovered as hydrofluoric acid. Solid iron and chromium fluorides, mainly K₂FeF₅(s) and CrF₃(s), obtained in the UCM treatment process, were employed in this work. Optimal hydrolysis operating conditions were obtained by means of a factorial design: media must be basic but pH cannot be higher than 9.5, temperature from 40 to 70 °C and alkali concentration (potassium hydroxide) below 1.1 mol L⁻¹. Secondary reactions have been detected, which are probably due to fluoride adsorption onto obtained oxides surface. Mechanism of reaction consists of several stages, involving solid fluoride dissolution and complexes decomposition. Hydrolysis kinetics has been modeled with classical crystal dissolution kinetics, based on mass transfer phenomena.

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1. Introduction

Fluoride chemistry in aqueous solutions in the presence of metal ions depends on complexes formation, as occurs for iron and chromium [1,2]. This highly influences on treatment processes for fluoride removal in drinking water [3] and industrial effluents [4]. Stainless steel pickling is one of the most important processes governed by fluoride complexes chemistry [5].

1.1. Stainless steel chemical pickling

Pickling is the removal of the oxides scale formed over steel surface, mainly produced by strains reduction in hot rolling or extrusion processes. In AISI 304 stainless steel case, oxides scale is composed of iron, chromium and nickel, with silica, manganese and molybdenum oxides traces. Main phases are wustite, magnetite, hematite and chromium(III) oxides with high resis-

tance to be solved in acid solutions [1]. Removal can be made by means of mechanical methods, as shot blasting, or electrolytic methods [6]. However, essential pickling process for better surface finishing is made in a chemical way by submerging steel sheets in hydrofluoric and nitric acids baths. Dissolution mechanism depends on oxidation reactions with nitric acid and catalyzed by Fe³⁺ [7]. Fig. 1 shows a simplified reaction scheme.

Hydrofluoric acid role is essential, as it bonds to excess Fe³⁺ forming fluoride complexes. It also dissolves silica, which is very tough to nitric acid action. Complexation by fluoride has very high influence on stainless steel pickling bath composition. In fact, use of hydrofluoric acid decreases residence time of steel sheets, although hydrogen fluoride vapors are formed, which mixes with gaseous emissions of pickling process, mainly NO_x and hydrogen.

Bath is exhausted when metal concentration rises up to 5% (w/w) of total liquid, even though this value depends on acid mixture and steel composition. Pickling rate progressively decreases to null values. At this point, bath must be withdrawn and substituted by fresh acid mixture. Exhausted bath is one of the most important environmental concerns in steel mills. Table 1

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Nomenclature

A_c	crystal surface area ($\text{m}^2 \text{L}^{-1}$)
C	molar concentration (mol L^{-1})
C_i	concentration of i (mol L^{-1})
C_{Me}	concentration of metals (iron + chromium) (mol L^{-1})
C_{OH}	concentration of hydroxyl groups (mol L^{-1})
$C_{\text{OH},0}$	initial concentration of hydroxyl groups (mol L^{-1})
C_s	surface concentration (mol L^{-1})
D_i	diameter of particles (m)
F	F -ratio value
F_0	critical F -value for 95% significance level
J	mole flux ($\text{mol m}^2 \text{min}^{-1}$)
k_L	global mass transfer coefficient ($\text{L m}^{-2} \text{min}^{-1}$)
$m_{\text{F},s}$	fluoride mass in solid phase (g)
m_0	initial amount of solid (g)
m_{ss}	initial suspended solid concentration (g L^{-1})
M_T	suspended solid concentration (g L^{-1})
\bar{M}	molecular weight (g mol^{-1})
N	stirring speed (revolutions per minute, rpm)
N_i	number of particles per volume unit (L^{-1})
$N_{\text{KOH,cons}}$	moles of consumed potassium hydroxide (mol)
r_{OH}	relative consumption of OH^-
R	correlation index
SPL	spent pickling liquor
T	temperature ($^\circ\text{C}$)
w_i	mass fraction of the i th interval of particle size
$x_{\text{F}}, x_{\text{Fe}}, x_{\text{Cr}}$	mass fraction of fluoride, iron and chromium in solid phase (w/w)
X_{F}	fluoride conversion (w/w)
Y_{F}	adsorbed fluoride to solid ratio (w/w)

Greek symbols

α	star level of factorial design
ρ_s	density of solid (kg m^{-3})

shows Spent Pickle Liquor (SPL) composition and real species distribution for each main compound [8]. These values were obtained by equilibrium modeling carried out by our research group. At least 72.0% of total fluoride is complexed, while only 27.3% is in the acid form. Free iron and chromium concentrations are very low if compared to metal complexes. Then, SPL

Table 1
SPL composition and real species distribution (percentage, mol/mol)

Nitrate (150 g L^{-1})		Fluoride (60 g L^{-1})		Iron(III) (40 g L^{-1})		Chromium(III) (10 g L^{-1})		Nickel(II) (5 g L^{-1})	
NO_3^-	98.7%	HF	27.3%	Fe^{3+}	2.8%	Cr^{3+}	0.0%	Ni^{2+}	99.9%
Others	1.3%	MeF_n^{3-n}	72.0%	FeF_2^+	5.9%	CrF_2^+	79.4%	Others	0.1%
		F^-	0.1%	FeF_3	10.5%	CrF_3	19.6%		
		Others	0.6%	FeF_4^-	58.9%	Others	1.0%		
				FeF_5^{2-}	19.6%		0.0%		
				Others	0.5%				
					1.8%				

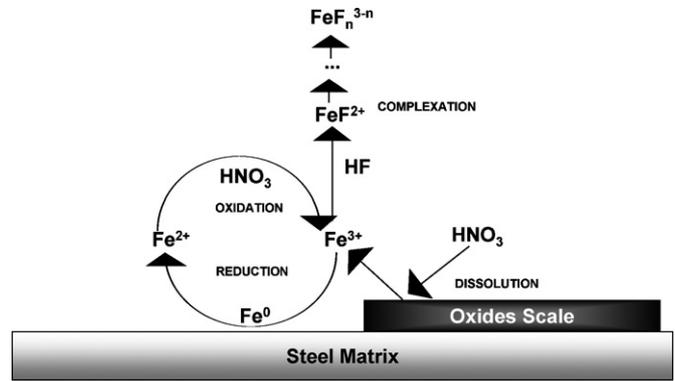


Fig. 1. Chemical pickling mechanism proposed by Ono et al. [7].

treatment processes are very dependent on complexes chemistry.

1.2. SPL treatment processes

SPL classical management consists of metals and fluorides neutralization and precipitation with lime. Metal hydroxides are obtained, while fluoride is removed as solid CaF_2 . The filter cake must be treated as a hazardous waste because of its heavy metals and fluoride content. During the last years, new treatment processes had been developed for SPL acid reclamation and, in few cases, metals recovery. The most widespread technique for free acid recovery is acid retardation [9]. This method and all others produce a metallic waste, actually a liquid effluent with solved metals and acid loss. As it is seen in Table 1, at least 72% of fed hydrofluoric acid to pickling process may be loss. Breakage of complexes and free hydrofluoric acid releasing are interesting in order to diminish fresh acid addition to pickling process and recycle metals to the metallurgical process.

1.3. Complex fluorides hydrolysis

As shown in Table 1, nickel hardly forms complexes with fluoride, while 99% of iron and chromium are forming stable compounds with this anion. Our research group in the Chemical Engineering Department of the Complutense University of Madrid has proposed a new process for nickel recovering [10], which is the most valuable metal, by splitting it from iron and chromium. This process consists of iron and chromium precipitation as fluoride, while nickel remains in solution and can be

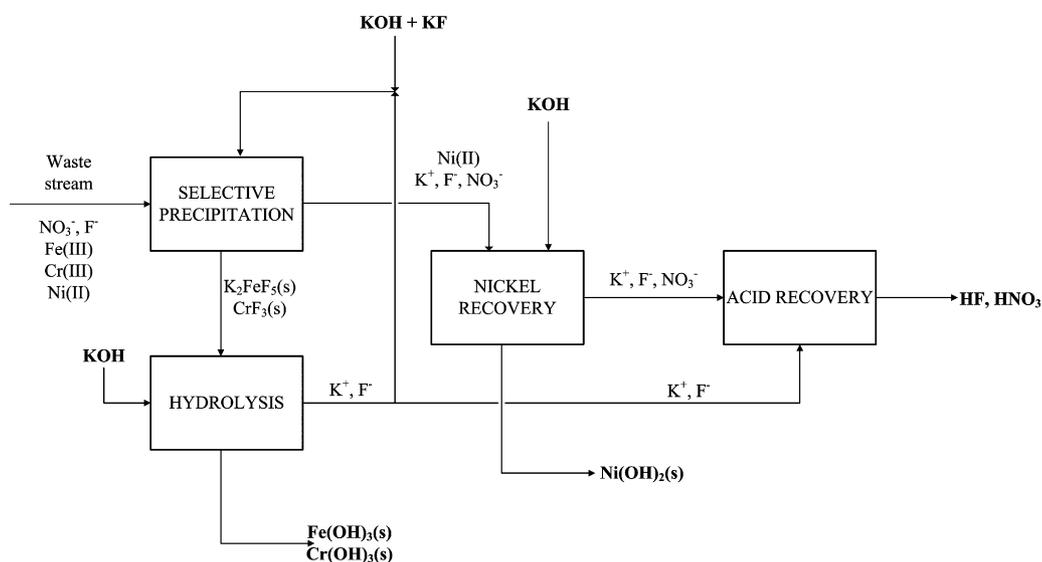


Fig. 2. Proposed process for SPL treatment.

recovered as high purity hydroxide in other stage. Block diagram of proposed process is presented in Fig. 2.

Process key is free fluoride addition (as potassium fluoride) for displacing equilibrium system to high F^- complexes establishment. Then, mixtures of K_2FeF_5 and CrF_3 are obtained as unique solid phases. If fluoride addition is not enough, iron and chromium oxides and hydroxides appear in solid phase. Then, nickel adsorption and coprecipitation may occur and decrease nickel recovery yield.

Mixtures of precipitated fluorides are not recyclable for the metallurgical process. So, they are hydrolyzed by alkali addition for precipitating metals as oxides and fluoride releasing. Reaction taking place for iron fluoride can be described as follows:



Hydrolysis of metal fluorides is usually made thermally, by reacting them with steam [11,12]. Main objective of this paper is to describe the influence of operational conditions on basic hydrolysis of fluorides in aqueous solution, which is simpler and more cost-effective than thermal way. Reaction mechanism is also studied, as well as reaction kinetics. Although these aspects are developed for K_2FeF_5 and CrF_3 , results may be applied for any other solid fluorides treatments, e.g. solids produced during pickling process as β - FeF_3 [13].

2. Materials and methods

2.1. Raw materials

Raw solid fluorides for experimentation were obtained in optimal conditions of selective precipitation stage [14]. Table 2 shows their main characteristics. It is remarkable the presence of trace metals coming from pickling liquors (Si, Mn, Mo, ...), while nickel, a major compound of stainless steel, is not detected in the analysis.

Although more than 95% of solid is composed of K_2FeF_5 and CrF_3 mixtures, a mean molecule is considered for calcula-

tion in molar basis. Particle size distribution is used for kinetics determination. Mean particle size will not be considered as a variable in the study due to the impossibility of controlling it without changing optimal operating conditions in the selective precipitation of fluorides. Moreover, particle classifying is not required because overall treatment of whole generated SPL is being achieved.

All other reagents were prepared with analytical purity provided by PANREAC.

2.2. Analytical methods

Liquid samples were filtered using a $0.45 \mu m$ microfilter. Fluoride was measured by a calibrated ion selective electrode (METTLER-TOLEDO). Hydroxide groups' concentration (OH^-) was measured by standardized titration with hydrochloric acid.

Table 2
Raw fluorides properties

Property	Value	
Composition (w/w)	F: 37.3%	Na: 0.5%
	K: 32.8%	Mn: 0.2%
	Fe: 17.1%	Ni: <0.01%
	O: 5.9%	Mo: <0.01%
	Cr: 4.0%	Cu: <0.01%
	Si: 0.3%	
Mean molecule	$K_{2.1}Fe_{0.8}Cr_{0.2}F_{5.1} \cdot 0.95H_2O$	
Mean molecular weight	255.1 $g \cdot mol^{-1}$	
Density	2310 $kg \cdot m^{-3}$	
Mean particle size	32 μm	
Particle size distribution (w/w)	1–2 μm	2.0%
	2–4.3 μm	8.7%
	4.3–9.3 μm	17.5%
	9.3–20 μm	25.0%
	20–43 μm	25.5%
	43–93 μm	15.7%
	93–200 μm	5.4%
200–430 μm	0.15%	

ric acid, using an automatic titrator (CRISON D++). Metals concentration was measured by atomic absorption spectrometry with a VARIAN SPECTRAA 220 equipment. Solid characterization was made by X-Ray Diffraction using a SIEMENS KRISTALLOFLEX 810 goniometer with Cu K α radiation.

2.3. Experimental procedure

Two main types of tests have been developed because of the difference between controlled pH and non-controlled pH. Controlled pH experiments were designed for optimizing experimental conditions tests and non-controlled pH were established for kinetic tests. Value of pH was not controlled in kinetic tests because high amounts of potassium hydroxide were added, so pH of solutions was higher than electrode sensitivity.

Experimental procedure when pH is controlled. Six hundred milliliters of water were introduced into a 2L reactor. HNO₃ was added to decrease pH down to 4 to inhibit initial hydrolysis reaction with water. Temperature was controlled by a thermostatic water bath, whose heater was connected to a PT 100 probe placed in reaction media. Eighty grams of raw solid were suspended homogeneously in reaction media by stirring with an anchor-type impeller. For that purpose, stirring speed must be higher than 250 rpm. A pH probe was placed contacting reaction media and connected to a pH-controller that ran a peristaltic pump to add basic agent (aqueous solution of potassium hydroxide) to the reactor. Chosen test time was 90 min. Reactor content was vacuum-filtered, collected solid was dried at 105 °C for its characterization and liquid samples were collected for fluoride content analysis. Potassium hydroxide solution addition was also measured as it is an analyzed response in this study.

Experimental procedure when pH is not controlled. Experimental installation was the same as in the previous case, but without control of pH. Reactor was charged with 1.2 L of aqueous solution of potassium hydroxide and heated at working temperature with thermostatic bath and heater. When solid was fed to reactor, time was set to $t = 0$. Samples were collected at 2, 5, 10, 15, 30, 45, 60 and 90 min for fluoride and OH⁻ analysis.

2.4. Methodology

2.4.1. Study on experimental conditions

Reaction (1) indicates each metal molecule needs at least 3 of potassium hydroxide ones. So, reaction media have to be highly basic in order to enhance fluorides conversion. This implies that pH must be considered as study variable. Other important variable is temperature as reaction between solid and liquid is influenced by mass diffusion. Potassium hydroxide concentration has no influence in pH media because it is controlled in these experiments, but has a significant influence on ionic strength of media and, consequently, changes the repulsion forces between suspended particles and fluoride releasing rate.

These three variables have been considered for a factorial design of experiments. Experimental levels were chosen after a previous set of short tests. These short tests were low volume hydrolysis (10 g of raw solid in 200 mL of water) achieved by automatic titration, feeding KOH 1 mol L⁻¹ solution to reaction

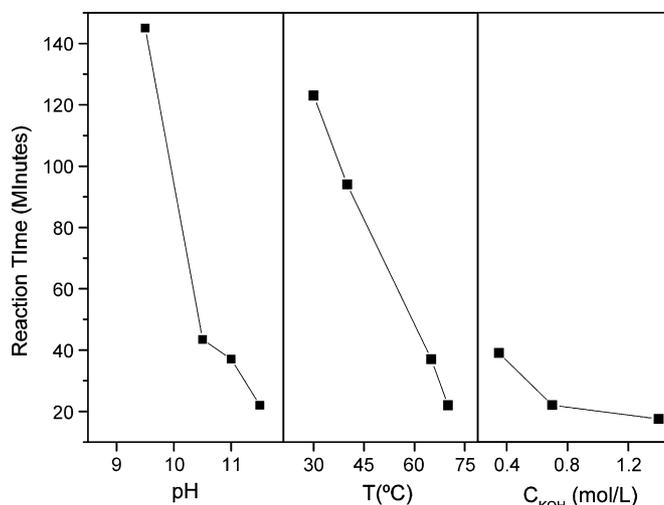


Fig. 3. Reaction time (minutes) vs. pH, temperature and potassium hydroxide concentration.

media. Titrator was programmed to give the time when pH was stabilized and there was not need for KOH addition. This time is the same as final reaction time because reaction is over when there is no OH⁻ consumption, hence pH does not vary. Variation of reaction time is observed in Fig. 3.

As Fig. 3 shows, pH has very high influence on reaction time due to pH indicates free OH⁻ concentration in solution. Experimental range of pH for optimizing experimental conditions was set from 9 to 11. Temperature induces hydrolysis, as seen in Fig. 3, so its experimentation range would cover from 40 to 70 °C, avoiding water evaporation because aqueous media is used in the process and total vessel pressure is approximately 1 bar. Potassium hydroxide concentration does not have as much influence as temperature and pH, but if it is increased, reaction time decreased. This fact implies that total ionic strength of solution has an important role in the process: when KOH concentration is augmented, ionic strength increases and fluoride releasing is retarded by counterions.

Selected levels for potassium hydroxide concentration were 1 and 3 mol L⁻¹, which are of high-concentration in order to avoid dilute free fluoride recovering. A linear regression was first assumed with 2³ + 4 central points. As analyzed responses showed a non-linear behavior, the factorial design was augmented to a non-linear rotatable 2³ design with star points located at $\alpha = 1.6818$ and 6 center points. Final levels and factors are shown in Table 3.

Analyzed response is chosen for reaction progress evaluation. Two responses are analyzed:

Table 3
Levels and values for each factor of the factorial design

Factor	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
T(°C)	30	40	55	70	80
pH	7	8	9.5	11	12
C _{KOH} (mol L ⁻¹)	0.3	1	2	3	3.7

Table 4
Levels and responses from the factorial design tests

Test	Levels			Values			Responses	
	pH	T (°C)	C _{KOH}	pH	T (°C)	C _{KOH} (mol L ⁻¹)	r _{KOH}	X _F
1	-1	-1	-1	8	40	1	0.11	0.09
2	+1	-1	-1	11	40	1	0.35	0.33
3	-1	+1	-1	8	70	1	0.15	0.17
4	+1	+1	-1	11	70	1	1.03	0.93
5	-1	-1	+1	8	40	3	0.35	0.36
6	1	-1	+1	11	40	3	0.42	0.44
7	-1	+1	+1	8	70	3	0.16	0.17
8	1	+1	+1	11	70	3	0.54	0.47
9	-α	0	0	7.0	55	2	0.25	0.11
10	+α	0	0	12.0	55	2	1.21	0.76
11	0	-α	0	9.5	30	2	0.19	0.12
12	0	+α	0	9.5	80	2	0.55	0.38
13	0	0	-α	9.5	55	0.3	0.51	0.40
14	0	0	+α	9.5	55	3.7	0.35	0.28
15	0	0	0	9.5	55	2	0.23	0.20
16	0	0	0	9.5	55	2	0.19	0.20
17	0	0	0	9.5	55	2	0.23	0.23
18	0	0	0	9.5	55	2	0.32	0.29
19	0	0	0	9.5	55	2	0.32	0.14
20	0	0	0	9.5	55	2	0.42	0.27

- Base consumption, r_{KOH} , is the ratio between moles of OH⁻ consumed in the reaction and theoretical consumption, taking into account a stoichiometric coefficient of 3 per metal mol in feed stream. Base consumption can be higher than 1, because any secondary reaction makes consumption to increase:

$$r_{OH} = \frac{N_{KOH,cons}}{3((x_{Fe}/55.8) + (x_{Cr}/52))m_0} \quad (2)$$

- Fluoride conversion is the same as solid conversion and it is defined as follows:

$$X_F = \frac{m_{F,s}}{x_F m_0} \quad (3)$$

Fluoride and KOH are product and reagent of reaction (1). If any other reaction does not take place, behavior of both responses must be the same as function of design factors.

2.4.2. Reaction kinetics

K₂FeF₅ and CrF₃ are obtained in the first precipitation stage of the proposed process (Fig. 1) with high concentration of crystalline phase (more than 90%). As fluoride must be dissolved from initial solid, probable reaction mechanism would depend on diffusion mechanism. Then, stirring speed and total surface area must be studied for kinetic modeling. Area has been calculated from particle size distribution and was varied by changing suspended solid concentration. Temperature and

Table 5
ANOVA test for X_F and r_{OH} responses

Effect/response	Sum of squares		Freedom degrees		Mean		F/F ₀		p-value	
	X _F	r _{OH}	X _F	r _{OH}	X _F	r _{OH}	X _F	r _{OH}	X _F	r _{OH}
pH	0.45	0.74	1	1	0.45	0.74	22.53	11.83	0.0001	0.0001
T	0.07	0.12	1	1	0.07	0.12	3.48	1.87	0.0049	0.0144
C _{KOH}	0.01	D	1	D	0.01	D	0.28	D	0.2285	D
(pH) ²	0.09	0.24	1	1	0.09	0.24	4.54	3.77	0.0028	0.0025
(pH·T)	0.07	0.11	1	1	0.07	0.11	3.44	1.83	0.0050	0.0152
(pH·C _{KOH})	0.05	0.06	1	1	0.05	0.06	2.42	0.92	0.0104	0.0573
(T) ²	D	D	D	D	D	D	D	D	D	D
(T·C _{KOH})	0.09	0.08	1	1	0.09	0.08	4.31	1.23	0.0031	0.0341
(C _{KOH}) ²	0.03	D	1	D	0.03	D	1.46	D	0.0267	D
Lack of fit	0.02	0.08	6	6	0.00	0.01	0.21	0.31	0.4898	0.4074
Pure error	0.02	0.08	5	7	0.00	0.01	-	-	-	-
Total (corrected)	0.87	1.50	19	19	-	-	-	-	-	-
R-squared	R ² (X _F)=0.932		R ² (r _{OH})=0.895							

D: discarded effect.

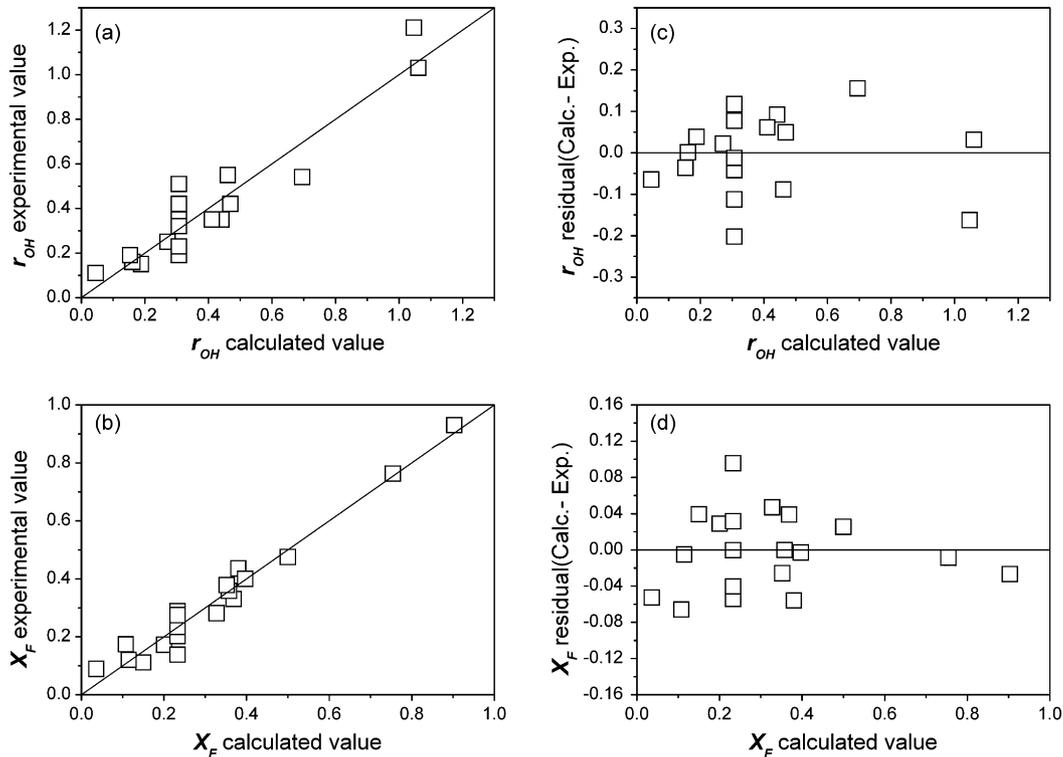


Fig. 4. Experimental vs. calculated value plots for (a) r_{OH} and (b) X_F . Residual vs. calculated value plots for (c) r_{OH} and (d) X_F .

potassium hydroxide concentration were also studied variables in this part.

3. Results and discussion

3.1. Study on experimental conditions

Levels and values of experimental factors for each test and obtained responses in the study on operating conditions are shown in Table 4. Analysis of variance is shown in Table 5 for each response, where F/F_0 and p -value are calculated for each measured effect, including interactions.

Discarded effects are those whose p -values are higher than 0.05 and F/F_0 lower than 1. However, C_{OH} effect has to be mathematically included in the analysis of fluoride conversion, X_F , due to the significant influence of the quadratic term, C_{KOH}^2 . Other doubtful, but included, effect is that from $pH \cdot C_{KOH}$ interaction on hydroxide consumption ratio, r_{OH} , since it becomes an important factor when significance level is established at 90%. Predicted statistic models for both responses are:

$$X_F = 2.61 - 0.67pH - 0.02T + 0.67C_{OH} + 0.035pH^2 + 0.004pHT - 0.052pHC_{OH} - 0.007TC_{OH} + 0.045C_{OH}^2 \quad (4)$$

$$r_{OH} = 0.31 + 0.47pH + 0.25pH^2 + 0.24pHT - 0.2TC_{OH} + 0.18T - 0.17pHC_{OH} \quad (5)$$

As seen in Table 5, squared-correlation index is high enough for both responses. Experimental value vs. calculated value and

residual vs. calculated value for both responses are shown in Fig. 4.

These plots show that model fits with accuracy experimental values, while residuals are distributed around the X-axis at random. Although there is a high concentration of data below $X_F = 0.5$ or $r_{OH} = 0.5$, the model integrates adequately the experimental results over 0.5 for X_F or r_{OH} .

Fig. 5 shows the influence of the variation of each factor in both responses. Potassium hydroxide consumption greatly increased when pH value augments. This implies that reaction kinetics is very influenced by OH^- concentration in the media,

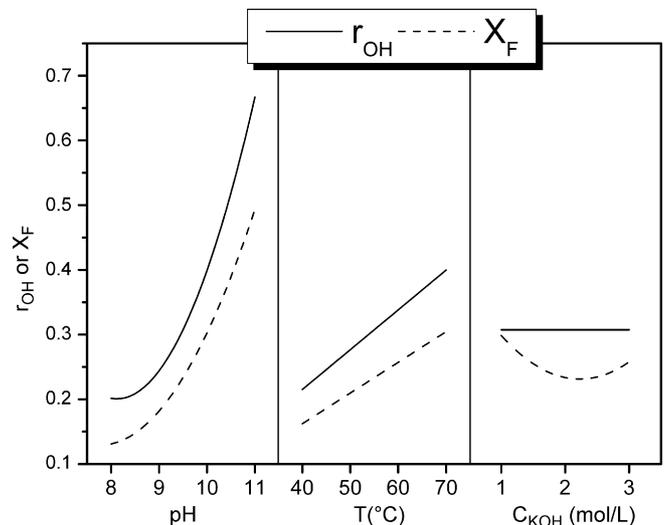


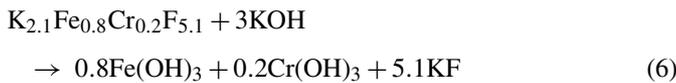
Fig. 5. Effects of experimental factors in r_{OH} and X_F .

producing high amounts of iron and chromium oxides. However, when pH decreases, still in a basic media, slope of the curve decreases achieving a null value at pH 7. Then, a minimum pH is required for destabilizing solid fluorides of iron and chromium, K_2FeF_5 and CrF_3 . The same behavior is observed for fluoride conversion, X_F , although values are lower.

Temperature has a positive influence on both responses. In one hand, this can be due to a kinetic effect on product generation (oxides or hydroxides formation and fluoride release to solution) and thus global reaction is endothermic. In the other hand, linear behavior of both models indicates that diffusion effects can be taking place. This fact will be proved in Section 3.3.

Potassium hydroxide concentration has no influence on OH^- consumption but has a negative quadratic effect on fluoride conversion. As this concentration has a direct influence on the ionic strength of reaction media, there is a negative secondary process that decreases fluoride releasing to solution. Electrostatic repulsion between OH^- and F^- by increasing ionic strength can occur, promoting fluoride adsorption to solid surface.

This effect can be confirmed by the difference between r_{OH} and X_F curves. As mean molecule is $K_{2.1}Fe_{0.8}Cr_{0.2}F_{5.1} \cdot 0.95H_2O$, the following reaction can be assumed:



Assuming reaction (6) is the only one taking place in reaction media, 100% conversion process, relationship between both responses is:

$$\frac{r_{OH}}{X_F} = \frac{N_{OH,cons} x_F m_0}{m_{F,dis} 3((x_{Fe}/55.8) + (x_{Cr}/52))m_0} = 1 \quad (7)$$

In experimental tests relationship r_{OH}/X_F is higher than 1. Looking at Eq. (7) the problem can be explained by two possibilities:

- Higher demand on OH^- than supposed due to higher stoichiometric coefficient for potassium hydroxide in reaction (6). This is highly improbable due to oxidation states of iron and chromium do not change during the reaction because oxides

precipitate very fast. If all Cr(III) content is assumed to change to Cr(VI) and iron to remain as Fe(III), relationship r_{OH}/X_F value would be increased only 10^{-4} , i.e. relationship value would change to 1.0001. Furthermore, the quantity of other metals in raw material is not enough to explain the difference $r_{OH} - X_F$.

- Lower quantity of released fluoride. As fluoride is always associated to metals in pickling liquors, compounds like FeF_2OH are probably to be formed. Nevertheless, this kind of compounds does not make r_{OH}/X_F relationship to change, because oxidation state of metal ions remains the same. So, the best explanation is a new interaction between formed solids and fluoride should be integrated in the hydrolysis concept, as adsorption phenomena of fluoride.

So, adsorption is an important secondary process that makes the process to retain fluoride in the solid phase. As the main objective of the process is to reduce fluoride content in solid phase in order to obtain recyclable compounds of iron and chromium, a new response must be analyzed. This new response is the fraction of initial fluoride which is adsorbed. Mathematically, it is calculated with the following expression:

$$Y_F = \frac{\text{Mass of adsorbed fluoride}}{\text{Mass of initial fluoride}} = \frac{m_{F,ads}}{x_F m_0} = r_{OH} - X_F \quad (8)$$

Y_F must be minimized in order to obtain an experimental region where mass of adsorbed fluoride is null. It is calculated with the statistic models obtained for r_{OH} and X_F by combining Eqs. (3), (4) and (8) and setting $Y_F = 0$. Therefore, experimental conditions where there is no fluoride adsorption can be calculated. Fig. 6 shows three-dimensional graphs with pH– T – C_{OH} values for $Y_F = 0$.

Optimal conditions are under surface of Fig. 6a. Potassium hydroxide concentration must be lower than 1.1 mol L^{-1} in order to maximize fluoride releasing to solution. Then, ionic strength of reaction media must be as low as possible (decreasing potassium hydroxide concentration or increasing dilution) in order to avoid fluoride contamination of solid phases. Influence of pH is also evident, since it has a direct effect on KOH consumption.

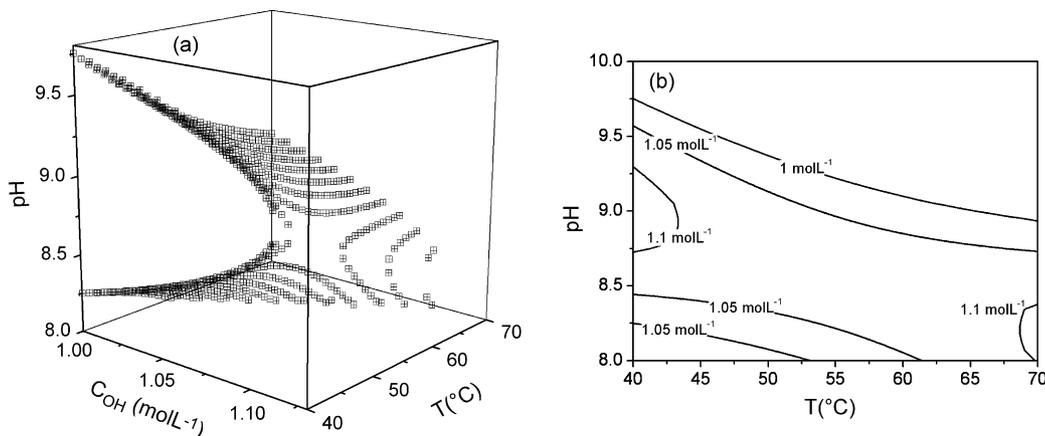


Fig. 6. (a) Detailed region of levels for each factor where Y_F is minimum, (b) contour levels of Fig. 6b for pH and T , with C_{OH} as curves parameter.

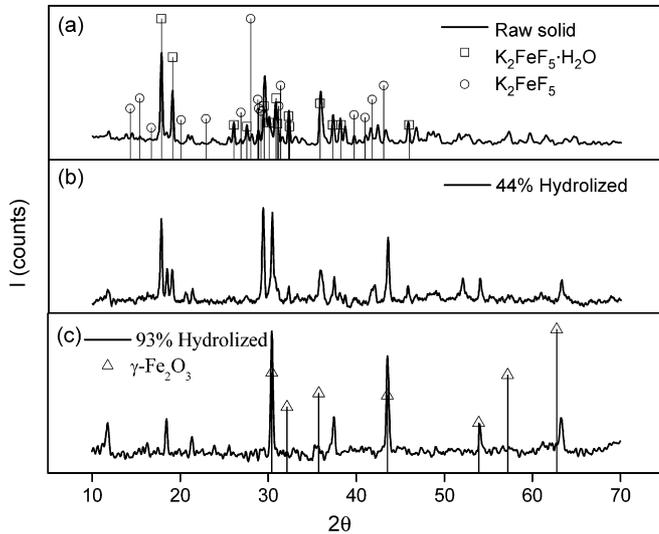


Fig. 7. Evolution of solid diffractograms: (a) initial solid, (b) solid obtained in test 7 and (c) solid obtained in test 4.

Temperature has no significant influence as minimum Y_F can be obtained in the whole experimentation range. However, it has a negative effect on optimal region limits, decreasing the value of pH boundaries when increasing operating temperature.

3.2. Reaction mechanism

Reaction mechanism is deduced from qualitative composition of solid phases from each test. Fig. 7 shows diffractograms of initial solid and obtained samples from tests 7 (44% conversion) and 4 (93% conversion). This figure allows studying the evolution of solid phases during reaction. Initial solid is composed mainly by K_2FeF_5 and CrF_3 , both in hydrated forms. Hydrolyzed solid is composed mainly by $\gamma-Fe_2O_3$, maghemite, polluted probably with $KFeO_2$, while chromium phase becomes undetectable in product diffractogram. When fluoride conversion is low, it is noticed that final solid is a mixture of both initial and hydrolyzed solid, as in its diffractogram there is a mixture of contribution from both phases. Then, intermediate solid phases do not exist and it is deduced that fluorides, e.g. K_2FeF_5 , are solved at basic pH, decomposing in K^+ and FeF_5^{2-} . Then, complex fluoride in solution decomposes in metal, Fe^{3+} , and fluoride ions, F^- . Released iron to solution is able to react with the basic agent (potassium hydroxide) to form iron oxide. The proposed general scheme and stages of the hydrolysis process are shown in Fig. 8.

The main stages of iron fluoride hydrolysis process, shown in Fig. 8, are:

1. Disintegration of molecule from crystalline structure and decomposition in ionic species.
2. Diffusion of ionic species through boundary limits surrounding each crystal particle in suspension.
3. Fluoride complexes decomposition, releasing free fluoride anion to solution, which stabilizes its charge with potassium cation.

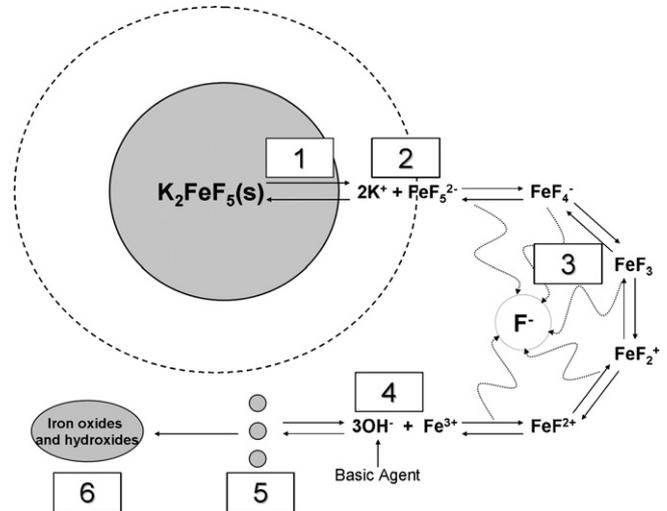


Fig. 8. Proposed hydrolysis mechanism for $K_2FeF_5(s)$.

4. Reaction of free iron, Fe^{3+} , in solution with hydroxyl groups formed in the basic media. The kinetics of this reaction is always very fast and tends to reach equilibrium concentrations.
5. Iron oxides precipitation and nucleation.
6. Iron oxides growth. Usually, this kind of oxides does not have an important growth step due to their high supersaturation ratio in solution.

In addition, it has to be remarked that secondary processes are taking place in parallel to reaction scheme shown in Fig. 8: fluoride adsorption to Fe_2O_3 and other oxides and potassium precipitation in combination with oxides as $KFeO_2$.

From stages 3–5, equilibrium reactions are quite fast. So, stages 1 and 2 are probably the controlling steps in the process, which are referred in literature as crystals dissolution [15] and are modeled in Section 3.3.

3.3. Reaction kinetics results

Hydrolysis of solid fluorides K_2FeF_5 and CrF_3 attends to a crystal dissolution process. As usual, in this kind of process, it is governed by a mass diffusion phenomenon which can be modeled by:

$$J = k_L(C_s - C_i) \quad (9)$$

where J is the mass flux, k_L is the global mass transfer coefficient, C_s is the metallic fluoride surface concentration and C_i is the metallic fluoride concentration in solution. The difference between C_s and C_i is the dissolution driving force, which can be powered if studied crystals differ very much from spherical shape.

Mass flux of dissolution process is defined as:

$$J = \frac{1}{A_c} \frac{dC}{dt} \quad (10)$$

where A_c is the crystal surface area per volume unit and dC/dt is the derivate of metallic fluoride concentration. In order to obtain

a more accurate model, surface area variation must be supposed and is function of crystal size distribution. As assumed in other models [15], mass fraction of each size interval is supposed to be constant while total crystals mass varies. For a time t , surface area is the sum of all crystals areas:

$$A_c = \sum_i^n N_i \pi D_i^2 \quad (11)$$

where i is the interval of particle size, D_i is the mean particle size in interval i and N_i is the number of crystals per volume unit. This last parameter is calculated by:

$$N_i = \frac{w_i M_T}{\rho_s (\pi/6) D_i^3} \quad (12)$$

where w_i is the mass fraction of particles in interval i , ρ_s is the solid density and M_T is the suspension concentration of solid that varies as a function of dissolved mass:

$$M_T = m_{ss} - \bar{M} C(t) \quad (13)$$

In Eq. (13), m_{ss} is the initial solid suspension concentration and \bar{M} is the molecular weight of solid. Metallic fluoride concentration must be calculated with a mass balance by assuming:

$$dC_{Me} = -\frac{1}{3} dC_{OH} \quad (14)$$

Then, value of C_{Me} is calculated as:

$$C_{Me} = \frac{1}{3} (C_{OH}^0 - C_{OH,t}) \quad (15)$$

Table 6

Values of studied variables for kinetic study of hydrolysis

Variable	Values
Temperature ($^{\circ}\text{C}$)	30, 40, 50, 60, 70
C_{OH}^0 (mol L^{-1})	0.4; 0.7; 1
m_{ss} (g L^{-1})	33, 50, 67, 83
Stirring speed, N (rpm)	100, 160, 200, 260

Eq. (14) establishes that OH^- consumption is equivalent to three-fold generated metallic fluoride concentration in solution, as metal content in solid is one atom per solid molecule (see Table 2) and oxidation state of chromium or iron remains III.

Fourteen experimental tests were planned for this section. Value of pH was not controlled because C_{OH} is an experimental factor of great interest. So, solid was introduced into a stirred potassium hydroxide solution with fixed temperature and concentration. Variables to be analyzed were potassium hydroxide concentration, suspended mass in solution, temperature and stirring speed. Response to be analyzed was the variation of C_{OH} with time, which was fitted to Eq. (16):

$$J = -\frac{1}{3A_c} \frac{dC_{OH}}{dt} = k_L \left(C_s - \frac{1}{3} C_{OH}^0 + \frac{1}{3} C_{OH} \right) \quad (16)$$

Values of experimental factors to be analyzed are shown in Table 6.

Fig. 9 shows the linear fitting of mass flux with C_{Me} . Linear regression fits well experimental data so there is no need

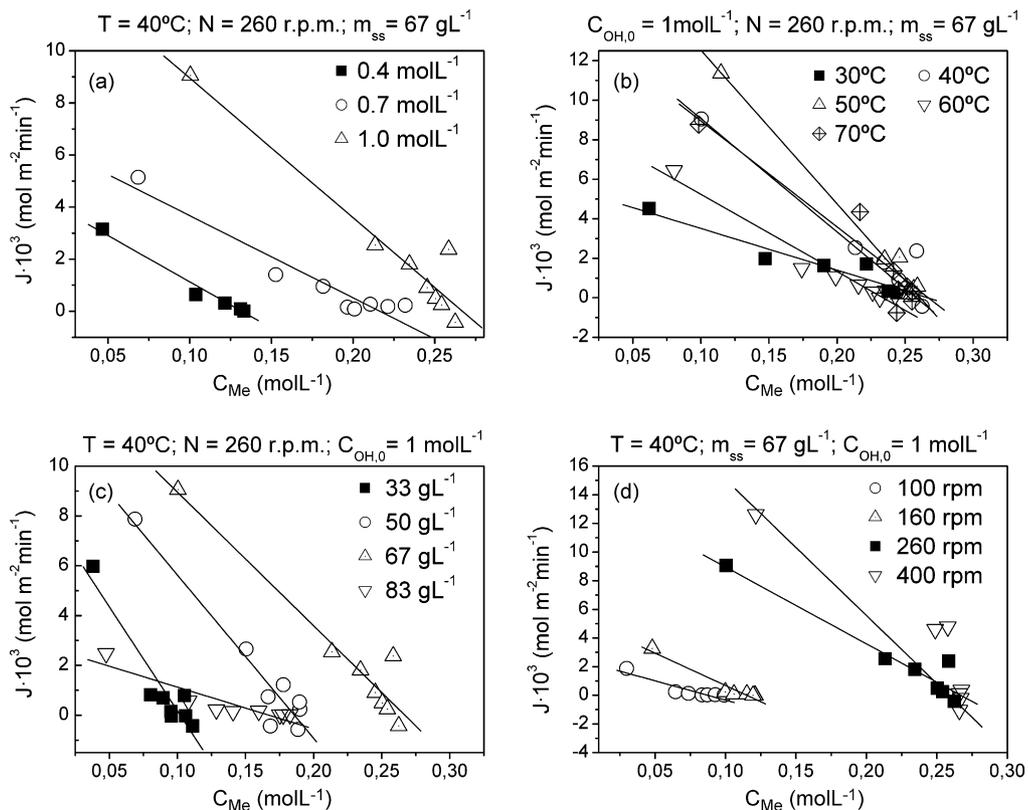


Fig. 9. Flux vs. solved complex concentration when (a) initial concentration of hydroxide, (b) temperature, (c) suspended solid concentration and (d) stirring speed are varied.

Table 7
Values of k_L and C_s for each test

Studied factor	Value	Operating conditions	$(k_L \pm \text{error}) \times 10^3 \text{ (L m}^{-2} \text{ min}^{-1})$	$(C_s \pm \text{error}) \times 10^2 \text{ (mol L}^{-1})$	R-squared
$C_{\text{OH},0}$ (mol L ⁻¹)	0.4	$T: 40^\circ\text{C}, m_{\text{ss}}: 67 \text{ g L}^{-1}, N: 260 \text{ rpm}$	35 ± 2	13 ± 2	0.997
	0.7		32 ± 4	22 ± 3	0.957
	1		54 ± 6	27 ± 3	0.897
T (°C)	30	$C_{\text{OH},0}: 1 \text{ mol L}^{-1}, m_{\text{ss}}: 67 \text{ g L}^{-1}, N: 260 \text{ rpm}$	21 ± 2	27 ± 4	0.858
	40		54 ± 6	27 ± 3	0.897
	50		70 ± 4	26 ± 1	0.920
	60		57 ± 8	23 ± 2	0.988
	70		39 ± 3	26 ± 2	0.973
m_{ss} (g L ⁻¹)	33	$T: 40^\circ\text{C}, C_{\text{OH},0}: 1 \text{ mol L}^{-1}, N: 260 \text{ rpm}$	83 ± 10	10 ± 3	0.999
	50		65 ± 8	19 ± 3	0.851
	67		54 ± 6	27 ± 3	0.897
	83		17 ± 2	17 ± 5	0.947
N (rpm)	100	$T: 40^\circ\text{C}, C_{\text{OH},0}: 1 \text{ mol L}^{-1}, m_{\text{ss}}: 67 \text{ g L}^{-1}$	27 ± 5	9 ± 2	0.930
	160		45 ± 5	12 ± 3	0.890
	260		54 ± 6	27 ± 3	0.897
	400		95 ± 10	26 ± 3	0.871

of a powered expression for Eq. (9). Linear behavior of mass flux is explained by the crystal dissolution process [15,16], as practically all crystals redissolve with a linear behavior of mass diffusion expression. From Eq. (15) is deduced that slope corresponds to mass transfer coefficient and $C_{\text{Me}}(J=0)$ is C_s . As observed in Fig. 9, slope varies with all studied factors, but C_s seems to be very similar for all temperatures and for high values of stirring speed (lines converge when $J=0$). This will lead to

similar values of parameters in both fitting vs. temperature and stirring speed.

Table 7 shows values of k_L and C_s for all experiments with the fitting error and squared correlation index shows the adequateness of the kinetic model.

As shown in Table 7, influence of temperature on mass transfer coefficients is positive. This corresponds to an increase of ion mobility with this factor. Nevertheless, surface concentration of

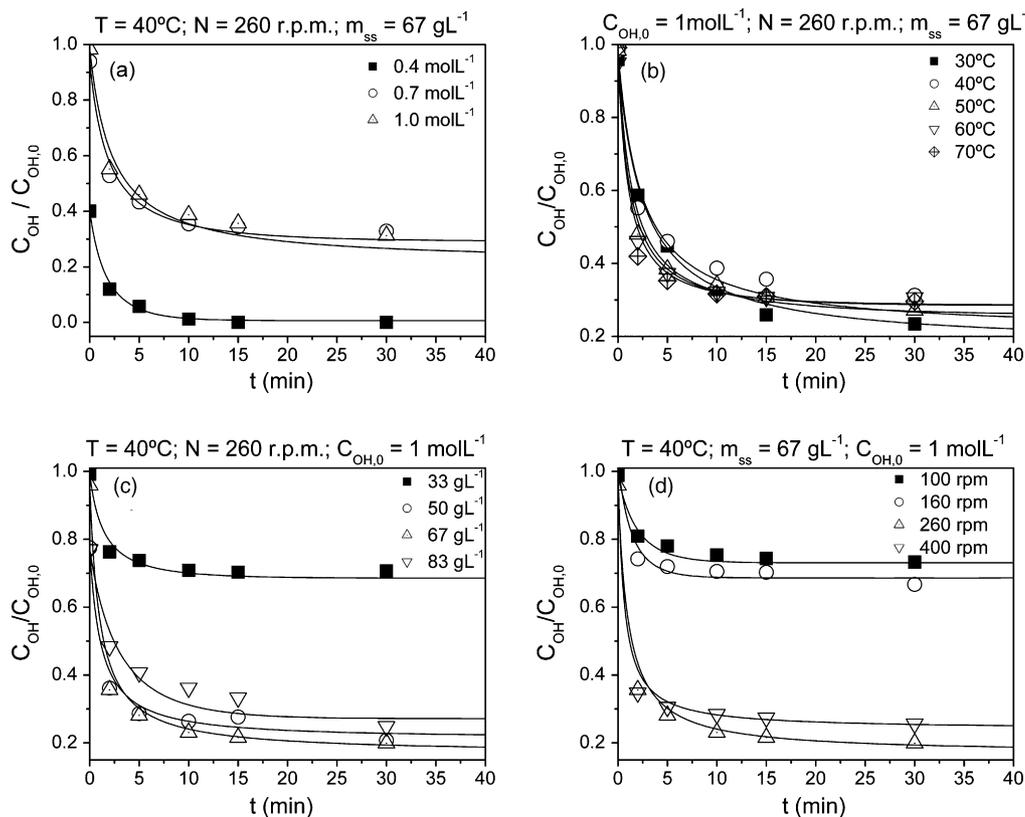


Fig. 10. Relative hydroxide concentration vs. reaction time when initial concentration of hydroxide (a), temperature (b), suspended solid concentration(c) and stirring speed (d) are varied.

solid is the same for all temperatures, showing that solubility of fluorides is very high when pH of reaction is strongly basic. In this case, C_s is not the solubility; its value is approximately the initial solid concentration in molar units, which is the maximum value of C_{Me} that can be reached.

Initial hydroxide concentration has a negative effect on mass transfer coefficient. This proves the conclusions from factorial design section: increasing concentration of media, provokes ionic strength rises and negative electrostatic repulsion effects can take place, delaying hydrolysis process. Surface concentration of metals is increased due to higher reactivity of metals with stronger basic media.

When stirring speed is increased better contact and turbulence is established in reaction media, so mass transfer coefficient augments. Surface concentration is also augmented, probably due to minimum stirring speed for homogeneous suspension is reached from 160 to 260 rpm, due to similarity of results for 260 and 400 rpm.

Suspended mass of initial solid has a negative effect on mass transfer coefficient because total area exposed to solution is increased and flux is decreased, as it is predicted from Eq. (16). However, surface concentration increases due to the high solubility and, then, maximum metal concentration in solution is the molar concentration of solid at the beginning of reaction, as in the temperature case.

Finally, Fig. 10 shows how the proposed kinetic model predicts experimental results in a very accurate way. Black lines represent calculated results for each experiment. So, kinetic model appears to be correct and crystal dissolution assumption is correct. Next research step would be the establishment of k_L correlations with experimental factors, suspension properties and reactor design parameters for a better understanding of reaction, design and scale-up of a hydrolysis, while secondary processes, as fluoride adsorption, should be modeled and considered for optimization of K_2FeF_5 and CrF_3 hydrolysis.

4. Conclusions

$K_2FeF_5(s)$ and $CrF_3(s)$ hydrolysis with potassium hydroxide is governed by a crystal dissolution process, as there is no intermediate solid product. Secondary reaction has been detected, unbalancing the theoretical mass balance of released fluoride. It has been supposed that fluoride salts are adsorbed to oxides products surface. In order to avoid adsorption, alkali concentration must be below 1.1 mol L^{-1} and pH below 9.5, while temperature does not have an important effect on adsorption, although it slightly changes pH limits of optimal conditions. Kinetics correspond to a linear mass transfer expression, as usual in crystalline compounds dissolution. Hydrolysis rate depends on temperature, surface area exposed to solution and potassium hydroxide

concentration, while there is a critical stirring speed (about 260 rpm) for maintaining a homogeneous solid suspension in reaction media.

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