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Y. D. Lai[a]; J. C. Liu[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL TAIWAN INSTITUTE OF TECHNOLOGY, TAIPEI, TAIWAN

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Fluoride Removal from Water with Spent Catalyst

Y. D. LAI and J. C. LIU*
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TAIWAN INSTITUTE OF TECHNOLOGY
TAIPEI, TAIWAN

ABSTRACT

The adsorption of fluoride from water with spent catalyst was studied. Adsorption density of fluoride decreased with increasing pH. Linear adsorption isotherm was utilized to describe the adsorption reaction. The adsorption was a first-order reaction, and the rate constant increased with decreasing surface loading. Adsorption reaction of fluoride onto spent catalyst was endothermic, and the reaction rate increased slightly with increasing temperature. Fluoro-alumino complex and free fluoride ion were involved in the adsorption reaction. It is proposed that both the silica and alumina fractions of spent catalyst contribute to the removal of fluoride from aqueous solution. Coulombic interaction is proposed as the major driving force of the adsorption reaction of fluoride onto spent catalyst.

Key Words. Adsorption; Aluminum; Fluoride; pH; Speciation; Spent catalyst; Temperature effect

INTRODUCTION

Spent catalysts contribute a significant amount of the solid wastes generated in the petrochemical industry. Hydroprocessing, reforming, and desulfurization all produce spent catalysts (1). In Taiwan, more than 3000 metric tons of spent catalysts are annually generated by a refinery. Spent

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* To whom correspondence should be addressed at Department of Chemical Engineering, National Taiwan Institute of Technology, 43 Keelung Road, Section 4, Taipei 10672, Taiwan. Telephone: 886-2-7376627. FAX: 886-2-737-6644. E-mail: liu@ch.ntit.edu.tw

catalysts are usually regenerated 2 to 3 times before they are wasted. Various technologies are available to refiners to handle these spent catalysts: use of spent catalysts as secondary raw material, disposal to land farming or land filling (2). Since spent catalysts consist mainly of porous silica and alumina, some research has focused on the feasibility of utilizing them as adsorbents to remove contaminants from water (3).

The major objective of the current study is to investigate the adsorption of fluoride by using spent hydroprocessing catalyst. Fluoride is commonly found in wastewater from fertilizer, glass, ceramic, phosphatic, petrochemical, and rubber industries (4). The presence of fluoride in certain aquatic systems has caused concerns. Reports on fluoride contamination can be found in the literature (5–10). The chronic health effect of excessive fluoride intake has been observed as skeletal abnormalities, dental fluorosis, and kidney disease (4). In Taiwan the maximum permissible limit of fluoride in drinking water is 0.8 mg/L and is 15 mg/L in industrial effluent. Previous studies show that fluoride in water and wastewater can be treated to a desirable limit by precipitation and adsorption (11) or by ion exchange (12). Lime and calcium salt precipitation of fluoride can practically reduce the residual fluoride concentration to 10 to 15 mg/L or even lower (11, 13). Adsorbents mostly used for fluoride removal include activated alumina, activated carbon, and clay (14–17). In the current study the feasibility of utilizing spent catalyst to remove fluoride from aqueous solution will be investigated. The equilibrium adsorption experiments will first be conducted, followed by adsorption kinetics study. Effects of important parameters, such as pH, surface loading, temperature, and solution chemistry, on fluoride adsorption will be explored.

MATERIALS AND METHODS

Spent hydroprocessing catalysts were obtained from the Research Institute of China Petroleum Corporation in Chia-Yi County, Taiwan. The specific gravity was determined to be 2.48 by the weight difference method. The specific surface area was determined to be 130 m^2/g by a BET specific area analyzer (Micromeritics ASAP 2000). The total organic carbon content was determined to be 455 mg/kg by a TOC analyzer (Astro 2001). The average size of spent catalyst was determined to be 11.3 μm by a sizer (Malvern 2600C). The size distribution of spent catalyst is shown in Fig. 1. Zeta potential of spent catalyst was measured by a zeta meter (Photal Leza-600) and is shown in Fig. 2. The isoelectric point (IEP) was found to be 5.2. Scanning electron microscope analysis (Cambridge S360) showed the surface of spent catalyst to be very porous (Fig. 3a). Semiquantitative surface content by energy-dispersive analysis showed (Fig.

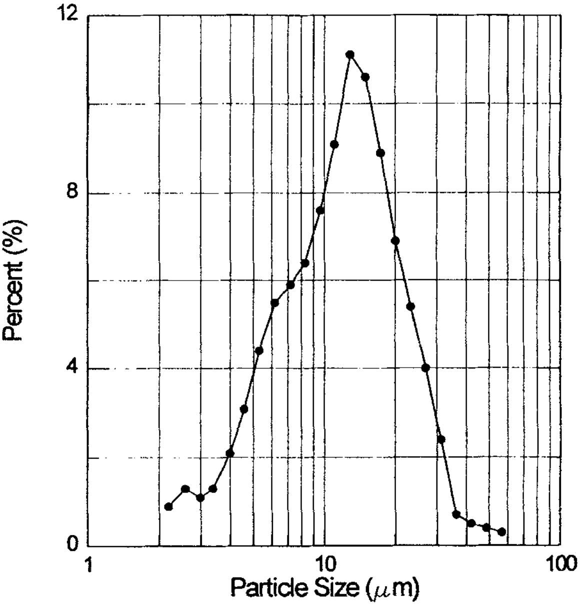

FIG. 1 Size distribution of spent catalyst.

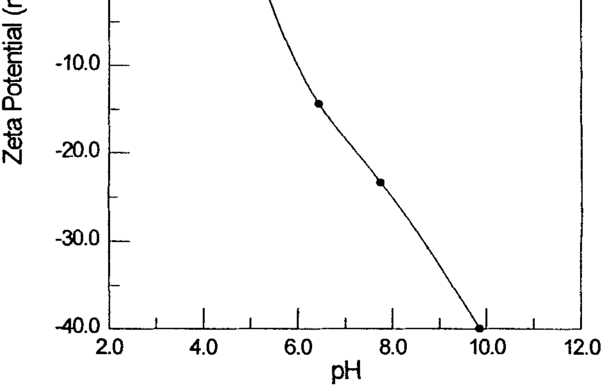

FIG. 2 Zeta potential of spent catalyst as a function of pH: ionic strength (I) = 0.05 N $NaNO_3$, solid concentration (S) = 10 g/L, 25°C.

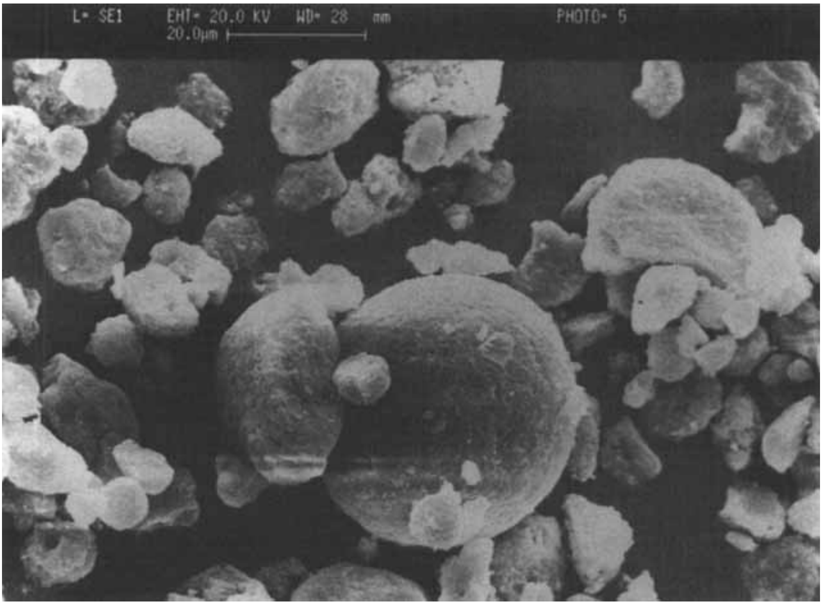

FIG. 3a Scanning electron microscope picture of spent catalyst.

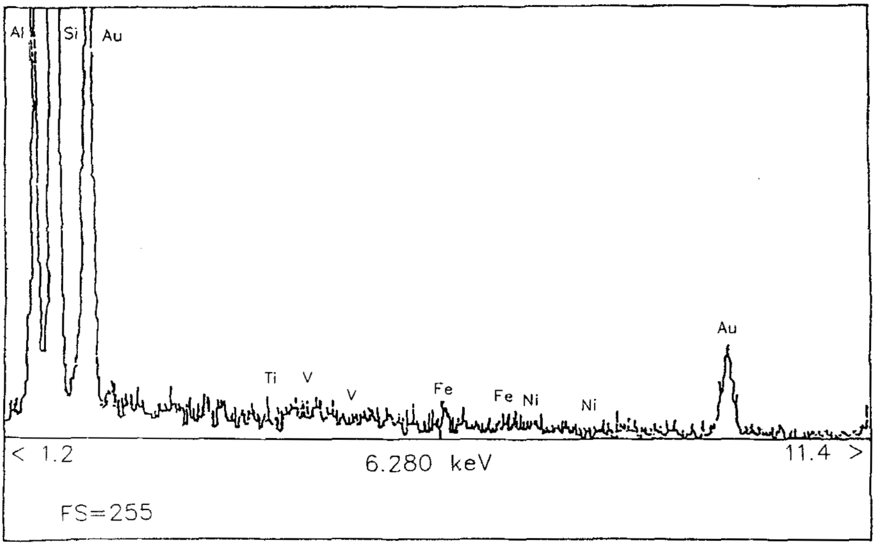

FIG. 3b Energy-dispersive spectrometric analysis of surface content of spent catalyst.

TABLE 1
Metal Contents of Spent Catalyst (mg/kg)

V	Cr	Fe	Co	Ni	Cu	Zn	Mo	Cd	Pb
4030	33.0	2000	12.3	1000	17.6	120	40	BDL[a]	18.7

[a] BDL: Below detection limit.

3b) that, apart from Si, Au, and Al, minor elements were Ti, V, Fe, and Ni.

To analyze the total metal content, 2.5 g of spent catalyst was put into a 250-mL Pyrex flask, 5 mL of 4 N HNO_3 was added to the spent catalyst, and then the mixture was placed on a heating plate (Corning PC-320) for digestion. A small amount of nitric acid was added intermittently to prevent spent catalyst from total dry-out until the supernatant became clear and a brownish-colored fume was no longer generated. The suspension was cooled and filtered through a 0.45-μm membrane filter (MFS) and then measured by an atomic absorption spectrophotometer (GBC 904). The results are summarized in Table 1. In order to examine the toxicity of spent catalyst, a TCLP (Toxicity Characteristic Leaching Procedures, EPA, Taiwan) experiment was conducted. 100 g of spent catalyst was first weighed and placed in a 2-L polyethylene bottle. An appropriate amount of extractant (acetic anhydride solution at a pH value of 2.88 ± 0.05) was added and then the mixture was placed on a rotary shaker (ATCS DC-20S) where it was rotated for 18 hours at 30 rpm. The spent catalyst suspension was then filtered through a 0.45-μm membrane filter (MFS). Concentrations of various metals in the filtrate were measured with an atomic absorption spectrophotometer. They are shown in Table 2. The results indicate the metal concentrations in the filtrate did not exceed the permissible limits, and the spent catalyst can be categorized as a nonhazardous waste.

Adsorption Experiments

To study the background concentration of fluoride of the spent catalyst, 1 g of spent catalyst and 100 mL of 0.05 N $NaNO_3$ aqueous solution were

TABLE 2
Metal Concentrations of TCLP Filtrate (mg/L)

V	Cr	Fe	Co	Ni	Cu	Zn	Mo	Cd	Pb
6.4	BDL	BDL	BDL	1.09	BDL	0.20	0.61	BDL	BDL

each put into a 125-mL polyethylene bottle, the pH of the suspension was adjusted with 1 N NaOH and 1 N HNO_3, and then the mixture was placed on a shaker (Firstek B603). After 48 hours of shaking the pH values of the suspensions were measured, and then they were filtered through 0.22-μm membrane filters (MFS). The fluoride concentrations were then determined by specific ion electrode (ASI). The results showed the background fluoride concentration was negligible throughout the pH range of 2–11. In order to investigate the complexation reaction between fluoride and aluminum ions, the dissolved concentration of aluminum at various pH values was measured with an atomic absorption spectrophotometer.

In the batch adsorption experiment on pH effect, adsorption reactions were carried out in 30-mL Pyrex glass tubes. The solid concentration was kept at 10 g/L. The ionic strength was adjusted to 0.05 M with $NaNO_3$. After the suspension pH was adjusted with 0.5 N HNO_3 and 0.5 N NaOH, the tubes were placed on a shaker and shaken for 12 hours. When the adsorption reaction was completed, the equilibrium pH values were measured and recorded. The suspension was filtered through a 0.22-μm membrane filter (MFS). The filtrate was then measured by a fluoride ion specific electrode (ASI). The amount of fluoride adsorbed was determined as the difference between the initial concentration and the equilibrium concentration. For the experiment on adsorption isotherm, the procedures were the same except that the pH values were kept at 4.0, 6.0, and 8.0, respectively.

For the experiment of surface loading on adsorption kinetics, 20 g of spent catalyst was added to a 2-L Pyrex reactor. The pH of the spent catalyst suspension in the reactor was kept at 4.0 ± 0.2, and the ionic strength was kept at 0.05 N $NaNO_3$. The suspension was continuously stirred at 150 rpm, throughout the experiment, and the temperature was kept at 25°C. Samples were taken at certain time interval. They were filtered through a 0.22-μm membrane filter (MFS) and measured for residual fluoride concentration. The procedures were then repeated except that the spent catalyst concentration was changed to 1 and 0.1 g/L, respectively. For the experiment on the temperature effect, the procedures were the same except that the reaction temperatures were controlled at 0, 25, and 50°C, respectively.

RESULTS AND DISCUSSION

Effect of pH on Fluoride Adsorption

The effect of pH on the adsorption of fluoride onto spent catalyst is illustrated in Fig. 4. The adsorption density of fluoride decreased as the pH shifted to the alkaline range, and a plateau was observed in the pH

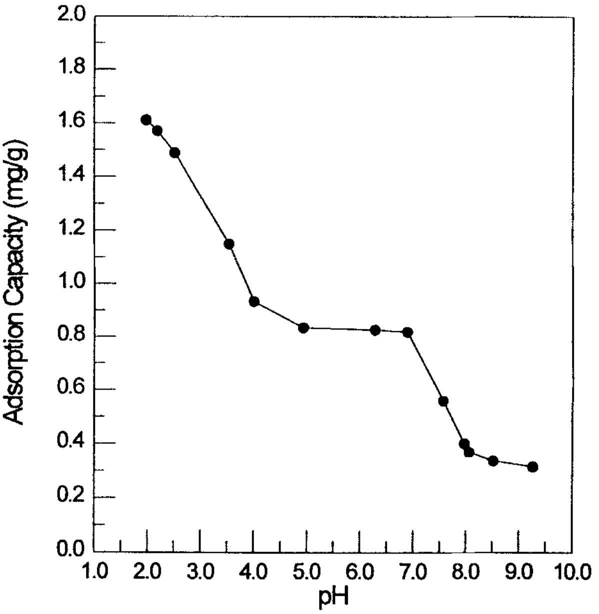

FIG. 4 Adsorption of fluoride as affected by pH: Initial concentration (C_0) = 20 mg/L, I = 0.05 N $NaNO_3$, S = 10 g/L, 25°C.

range of 4.0 to 7.0. Three adsorption isotherms of fluoride onto spent catalyst are shown in Fig. 5. The adsorption density of fluoride was highest at pH 4.0. The adsorption decreased slightly at pH 6.0, and decreased significantly when the pH was 8.0. A linear adsorption isotherm was utilized to model the adsorption reaction. The results are shown in Table 3.

Effect of Surface Loading on Fluoride Adsorption

Removal of fluoride under three different surface loadings was examined. It was observed that the adsorption of fluoride onto spent catalyst was very rapid. Most reactions were 70% completed within 10 minutes. The reaction rate increased with decreasing surface loading. The reaction was simulated by the differential method, assuming a first-order reaction rate. The results are shown in Table 4. It was found that the lower the surface loading, the higher the reaction rate, as well as the higher removal percentage. Yet, the adsorption capacity increased with increasing surface loading. This is consistent with previous findings on the adsorption reaction (18). Compared with results from previous work, the fluoride adsorp-

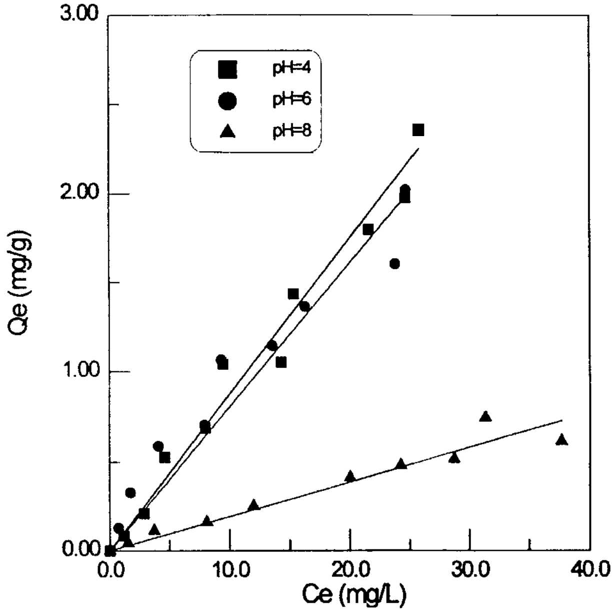

FIG. 5 Adsorption isotherms of fluoride onto spent catalyst at three different pH values: I = 0.05 N $NaNO_3$, S = 10 g/L, 25°C.

tion capacity of spent catalyst is approximately half to one-third of the capacity of activated alumina (15, 16).

Effect of Temperature on Fluoride Adsorption

The adsorption of fluoride onto spent catalyst under three different temperatures was studied. The adsorption density of fluoride increased when the temperature was raised from 5 to 25°C. Yet, little enhancement of

TABLE 3
Adsorption Constants of Fluoride onto Spent Catalyst by Utilizing Linear Adsorption Isotherm

pH	$Qe = KC_e$	γ^2
4.0	$Qe = 0.087C_e$	0.993
6.0	$Qe = 0.080C_e$	0.974
8.0	$Qe = 0.019C_e$	0.978

TABLE 4
Adsorption Rate Constants of Fluoride onto Spent Catalyst at Three Different Surface Loadings

Surface loading (mg/g)	Q_m[a] (mg/g)	K (min^{-1})
200	28.0	0.022
20	4.8	0.062
2	0.7	0.104
20[b]	10.0	0.006
19[c]	15.0	—

[a] Adsorption density after 30 minutes of reaction.
[b] Adsorption onto activated alumina (15).
[c] Adsorption onto activated alumina (16).

adsorption was found when temperature was further increased from 25 to 50°C. This shows the adsorption reaction to be endothermic. Meanwhile, the reaction rate increased only slightly with increasing temperature. The reaction was simulated by the differential method, assuming a first-order reaction rate. The results are shown in Table 5. The activation energy was calculated to be 3.2 J/mol by using the Arrhenius equation.

Based on the facts that the reaction is endothermic and the activation energy is very low, it can be concluded that the heat of reaction is also very low. Nonspecific interactions are possibly the driving force of fluoride adsorption onto spent catalyst.

Mechanism of Fluoride Adsorption onto Spent Catalyst

In order to elaborate on the adsorption mechanism, a dissolved concentration of aluminum from spent catalyst was measured and is shown in Fig. 6. The dissolved concentration of aluminum was ca. 97 mg/L at low pH. It decreased to 20 mg/L at pH 4.0. Only a very low concentration of

TABLE 5
Adsorption Rate Constants of Fluoride onto Spent Catalyst at Three Different Temperatures

Temperature (°C)	Q_m[a] (mg/g)	K (min^{-1})
5	18.0	0.019
25	28.0	0.022
50	28.0	0.023

[a] Adsorption density after 30 minutes of reaction.

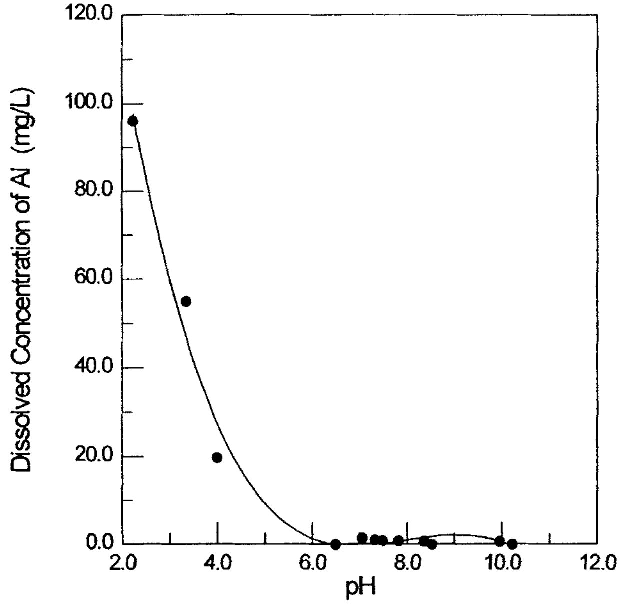

FIG. 6 Dissolved concentration of aluminum as affected by pH: I = 0.05 N $NaNO_3$, S = 10 g/L, 25°C.

aluminum was detected in the aqueous phase when the pH was higher than 6.4. Taking into account the complexation reaction between dissolved aluminum and fluoride ions, a computer software program, GEOCHEM (19), was utilized to calculate the chemical speciation of fluoride at different pH values. The results are shown in Fig. 7. The complexation reaction was very significant under acidic conditions. When the pH is lower than 4.8, most of the fluoride exists as a chemical complex with aluminum. The fluoro-alumino complex, $AlF_n^{(3-n)}$, is positively charged according to the stoichiometry. This fluoro-alumino complex fraction of fluoride then decreases rapidly between pH 4.8 and pH 6.0. Free fluoride ion becomes the dominant species when the pH is higher than 6.0.

Previous works (4, 17) have indicated the coulombic force between the positive charge of alumina and fluoride is the major driving force of the adsorption reaction. The coulombic force is still the major driving force in the adsorption of fluoride onto spent catalyst. This is supported by our finding that the heat of reaction is very low. Judging from the results of zeta potential, hydrous spent catalysts are positively charged when the pH is lower than an IEP of 5.2. However, the dominant species under

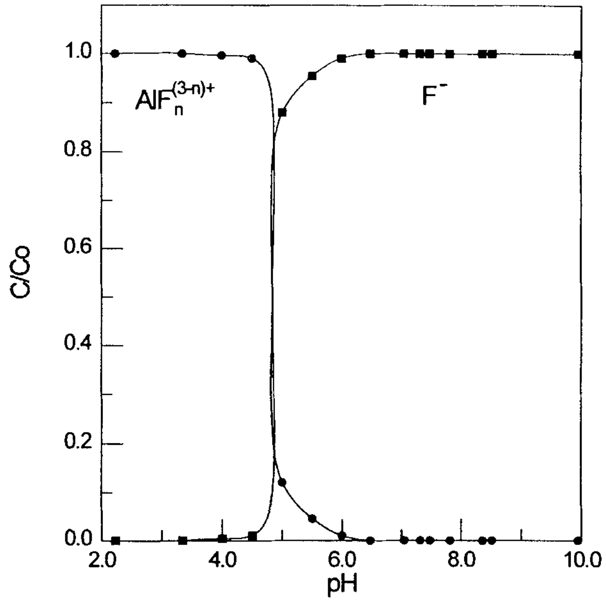

FIG. 7 Chemical speciation of dissolved aluminum and fluoride ions predicted by GEOCHEM: C = concentration of species, C_0 = total concentration, I = 0.05 N $NaNO_3$, S = 10 g/L, 25°C.

acidic conditions, the positively charged fluoro-alumino complex, cannot be adsorbed onto the alumina portion through the coulombic force. Therefore, both free fluoride ion and fluoro-alumino complex may be involved in the adsorption reaction. On the adsorbent side, the major components of the spent catalyst, silica and alumina, may both be involved. The surface charge of spent catalyst is contributed by the two determining portions (20). Additionally, the IEPs of silica and alumina are 2.0 and 8.3, respectively (21), and the electrical properties of the spent catalyst surface can theoretically be divided into finer sections (Fig. 8) because the silica fraction was positively charged when the pH was lower than 2.0, and negatively charged when the pH was higher than 2.0. Similarly, the positively charged alumina fraction was dominant when the pH was lower than 8.3, and the negatively charged alumina fraction became dominant when the pH was higher than 8.3. Depending on the pH values, different species from solution and spent catalyst participated in the adsorption reaction. The coulombic force between the silica fraction of spent catalyst and $AlF_n^{(3-n)}$ is the major driving force when the pH is lower than 4.8,

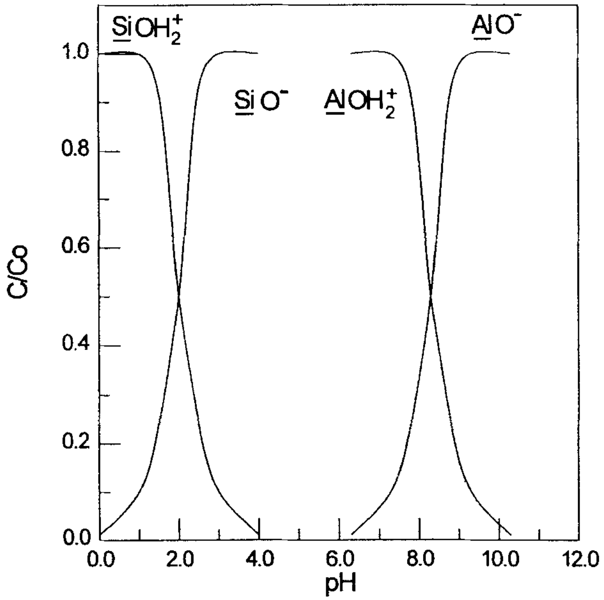

FIG. 8 Chemical speciation of silica and alumina fractions on hydrous spent catalyst surface as affected by pH.

while the coulombic force between alumina and free fluoride ion plays a more significant role when the pH is higher than 4.8. This proposed mechanism for fluoride removal agrees well with the adsorption data.

SUMMARY

The feasibility study of utilizing spent hydroprocessing catalyst to remove fluoride from aqueous solution leads to the following conclusions:

1. Spent catalyst can potentially be utilized as a secondary adsorbent in removing fluoride from aqueous solutions. The adsorption capacity is comparable to that of activated alumina.
2. The adsorption density of fluoride onto spent catalyst decreases with increasing pH. The linear adsorption isotherm fits the adsorption reaction well.
3. The adsorption reaction rate decreases with increasing surface loading. However, the adsorption capacity increases with increasing surface loading. The adsorption capacity of spent catalyst is comparable to that of activated alumina.

4. The adsorption reaction is endothermic, and the activation energy is very low. The heat of reaction is estimated to be very low. Consequently, a specific interaction does not appear to be involved in the adsorption reaction.
5. It is proposed that a fluoro-alumino complex and free fluoride ions are involved in the adsorption reaction. Additionally, both silica and alumina fractions of spent catalyst contribute sites for the adsorption reaction to occur. Coulombic force is the major driving force.

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