

Characterisation of selected South African clays for defluoridation of natural waters

PP Coetzee^{1*}, LL Coetzee², R Puka¹ and S Mubenga¹

¹Department of Chemistry and Biochemistry, ²Department of Geology, Rand Afrikaans University, PO Box 524, Auckland Park 2006, South Africa

Abstract

In large parts of South Africa groundwater contains excessive fluoride. In many such areas fluorosis is a serious problem among the local population. One way of solving the problem is to use simple house-based defluoridation systems using suitable clays, processed in various ways, as adsorbents. No information on the fluoride removal capacity of South African clays and soils is currently available. This study assesses the fluoride adsorption characteristics of clays selected from areas, such as the western Bushveld, where high fluoride concentrations in groundwater is a problem. Bauxitic clays were found to have the best overall potential as fluoride adsorbents. South African bauxite deposits, however, are not only low grade but are also to be found far from the problem areas in the North-West Province. Simple chemical activation using 1% Na₂CO₃ solutions and dilute hydrochloric acid could enhance adsorption capacity of certain clay types.

Keywords: defluoriation, fluorosis, fluoride adsorption, South African clay

Introduction

The occurrence of high fluoride concentrations in groundwaters and the risk of fluorosis associated with using such water for human consumption is a problem faced by many countries, notably India, Sri Lanka, China, the Rift Valley countries in East Africa, Turkey, and parts of South Africa. Fluorosis is a debilitating disease caused by drinking water with fluoride concentrations higher than ca. 1 mg·L⁻¹ for extended periods. The disease is characterised by mottled teeth in dental fluorosis and brittle bones in severe skeletal fluorosis. Much research has been carried out during the last 20 years to find cost-effective and practical solutions for the removal of excess fluoride from groundwater. In a recent report McCaffrey and Willis (2001) discussed the fluoride geochemistry of the North-West Province, one of the areas in South Africa where fluorosis is a problem. They focused attention on a serious problem faced by many rural communities which depend on borehole water with a high fluoride content for their drinking-water requirements. Affected areas include large parts of the Karoo, the Northern Cape, Limpopo, and North-West provinces. More than 30% of the ca. 3 000 boreholes in the Pilanesberg and western Bushveld area have fluoride concentrations > 1 mg·L⁻¹. In alkaline waters (pH > 9) fluoride concentrations up to 30 mg·L⁻¹ were recorded. The seriousness of the problem is exacerbated by evidence for a much lower safe maximum fluoride level in hot dry areas where the daily intake of water is much higher than normal. Brouwer et al. (1988) estimated that the maximum safe fluoride level in hot dry areas should be < 0.6 mg·L⁻¹. This value is confirmed by an empirical formula developed by Foss and Pittman (1986), which can be used to estimate safe limits for drinking water as a function of average temperature. At an average temperature of 28.5°C, typical for the North-West Province, the equation estimates a threshold fluoride concentration of 0.6 mg·L⁻¹, a value much lower than the 1.5 mg·L⁻¹ of the South African Drinking Water Standard.

* To whom all correspondence should be addressed.

☎ +2711 489-2558; fax: +2711 489-2819; e-mail: ppc@rau.ac.za
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Excellent technologies for defluoridation are available based on using activated alumina or reverse osmosis, but these technologies are not always applicable in rural areas due to financial and technological constraints. Taking into consideration that the estimated capital cost for defluoridation amounts to ca. R5 000 for a 50 L per day unit, based on either of these processes (Schoeman and Steyn, 2000), affordable alternatives, which would be easy to operate and which could be the basis for a house-based or do-it-yourself system, will have to be found. Various methods have been proposed ranging from adsorption on the inner walls of clay pots (Moges et al., 1996) in certain African countries to columns filled with clay brick chips in Sri Lanka (Padmasiri, 1991). Fluoride adsorption onto soils and clays have been studied extensively (Srimurali et al., 1998; Wang and Reardon, 2001) in practically all countries where the problem occurs. In general it was found that the adsorption capacity of soils and the clays was low and kinetics slow. Nevertheless, clay-based systems for defluoridation are used or are under investigation in many parts of the world.

South African clays and soils have not yet been assessed for their potential use as sorbents in house-based defluoridation systems. The purpose of this study was to investigate the adsorption characteristics of South African clay types and to assess their potential as adsorbents for simple defluoridation systems. In addition, the possible enhancement of adsorption capacity by simple physical and chemical pretreatment or activation procedures was investigated.

Clays as sorbents for fluoride

The term clay is often used in a non-specific way and could refer to: (a) soil consisting of a range of small particle sizes (eg. particle size < 1/256 mm on the Udden-Wentworth scale), (b) very fine-grained earthy substances comprising a combination of minerals, inorganic amorphous material and organic matter or (c) a specific clay mineral. The *clay minerals* are minerals in the phyllosilicate mineral group and as the name implies (Greek: *pyllon*, leaf), most of these minerals have a platy habit.

In this study the term clay refers to naturally occurring, very



Figure 1(a)

Major clay deposits (Horn and Strydom, 1998) and bauxite deposits (Barnardo, 1998) in the northern parts of South Africa

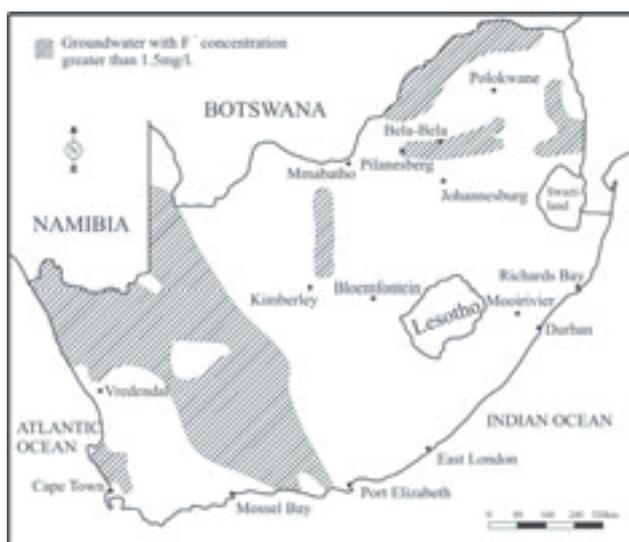


Figure 1(b)

South African groundwater F^- concentration $> 1.5 \text{ mg/l}$ (McCaffrey and Willis, 2001)

fine-grained earthy material composed primarily of clay minerals. Clays are potentially good adsorbers of anions since they contain crystalline minerals such as kaolinite, smectite and amorphous minerals such as allophane and other metal oxides and hydroxides which could adsorb anions such as F^- . The South African clay deposits shown in Fig. 1(a), can be broadly classified according to the dominant clay mineral present, into (1) Kaolin Fields (dominant clay mineral being kaolinite) (2) Bentonite Fields (dominant clay mineral being montmorillonite, which is part of the smectite group) and (3) Palygorskite Fields (dominant clay mineral being palygorskite). Bauxite, which is a rock type composed of one or

more of the aluminium hydroxides gibbsite, boehmite or diasporite is potentially also a good adsorber of anions and therefore the Bauxite Fields of South Africa have also been included in this study. Finally, the rock type laterite which represents a group of deposits consisting of residual insoluble ferric and aluminium oxides, clay minerals and quartz, formed by weathering of rocks, has also been included in this study as a potential adsorber of anions.

The structure of the clay plays a very important role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. In general the more negative the surface the better the sorption will be for positively charged metal ions. The pH parameter plays a dominant role in determining the adsorption capacity as pH modifies the charges on edge positions in phyllosilicates and also those of variably charged minerals such as gibbsite, hematite and goethite. Charges are generally positive under acid conditions and negative in an alkaline environment. The specific pH range for positive and negative surface charge will of course be a function of the pK_a values of the metal hydroxides present. An acid pH will favour adsorption of negatively charged ions while alkaline conditions will enhance adsorption of positive ions.

Many studies report on the fluoride adsorption capacities of clays and soils and their potential use as sorbents. The first comprehensive study of fluoride adsorption onto minerals and soils was published in 1967 (Bower and Hatcher, 1967). The results showed that excess fluoride in water could be removed to different degrees by adsorption onto a variety of soil and mineral types, in particular aluminium hydroxides. It was found that the adsorption is concentration-dependent and can be described by a Langmuir isotherm. Adsorption is typically followed by the release of OH^- ions.

Since the above paper had been published, fluoride adsorption studies were conducted in many countries and on a variety of soil and clay types such as: Illinois soils in the USA (Omueti and Jones, 1977), sodic soils in India (Chhabra et al., 1980), activated alumina (Hao et al., 1986; Schoeman and MacLeod, 1987), clay pottery (Chaturvedi et al., 1988; Hauge et al., 1994), Ando soils in Kenya (Zevenbergen et al., 1996), fired clay chips in Ethiopia (Moges et al., 1996), fly ash (Chaturvedi et al., 1990), kaolinite (Kau et al., 1997), and illite-goethite soils in China (Wang and Reardon, 2001).

Experimental

Sampling and selection of clay samples

In selecting the clay types for this study, two criteria were considered:

- The clay structure most likely to have good fluoride adsorption properties, i.e. hydroxyl-containing minerals and clays high in aluminium and iron oxides or hydroxides such as gibbsite and goethite/hematite minerals.
- The best possible clay deposits with potential fluoride adsorption properties in the areas where high-fluoride groundwaters are used for drinking-water and where fluorosis was demonstrated to be endemic. Although large parts of South Africa are at risk, this study focused on the western Bushveld area because it has been extensively studied (McCaffrey and Willis, 2001) with regard to the fluoride geochemistry and the distribution of fluoride in groundwater. Clay deposits situated within 500 km of the endemic area were identified and sampled for this study.

Known major clay deposits in South Africa were identified from geological maps and are shown in Fig. 1(a). The areas of high fluoride

TABLE 1
Descriptions and localities of samples examined during this study

No	Name	Description	Location
Kaolin clays			
1	ZEB1	Pure white clay from open pit.	Zebediela Kaolin Field (Fig. 1a) <i>Farm:</i> Rooiboschbaak 107KS
2	ZEB2	White clay with greenish tint, from open pit.	
3	ZEB6	Blood red clay, from open pit.	
4	RNF	Finely laminated orange and white clay in pan, 1 m to 2.5 m deep. Derived from weathering of Timeball Hill Shale.	Koster area <i>Farm:</i> Renosterfontein 494JP
Palygorskite clays			
5	LW1	Light brown colour, under 800 mm of black topsoil, 800 mm - 950 mm deep.	Modimolle area, Springbok Flats <i>Farm:</i> Leeuwaarden 633KR
6	CAL	Light brown clay from open pit. Below calcrete bed, ±12 m deep. Weathering product of basalt.	Immerpan Palygorskite Field (Fig. 1a) <i>Farm:</i> Calais 563KS
7	DB1	Blue-white clay sampled at base of open pit approximately 5 m deep.	Dwaalboom Palygorskite Field (Fig. 1a) Artherstone Nature Reserve, obtained from G&W Base and Industrial Minerals
8	DB2	White clay bed, 1.2 m thick, below approximately 500 mm black topsoil.	
Bentonite clays			
9	BEN	Bentonite sample - dry and finely milled product, greenish colour.	Koppies Bentonite Field (Fig. 1(a)) Obtained from G&W Base and Industrial Minerals
10	BBK2	Black clay, 50 mm to 300 mm deep, in shallow depression or pan.	Pienaarsrivier area, Springbok Flats <i>Farm:</i> Blaawboschkuil 20JR Bela-Bela
11	CF3	Main white clay bed, approximately 2 m thick. From open pit.	Naboomspruit area, Springbok Flats <i>Farm:</i> Cyferfonteine
12	CF4	Main red clay bed, approximately 2 m thick. From open pit.	
13	NHM	Black clay, 2.00 m - 2.5m deep.	Northam area
Laterites and bauxites			
14	LAT	Laterite, orange-red in colour, below 600 mm brown topsoil.	Pilanesberg area
15	PTA-LAT	Laterite. Orange-red colour.	Pretoria area
16	BAUX1	Orange colour and surface texture that resembles a human brain "Brainstone".	Howick area <i>Farm:</i> Lyndhurst
17	BAUX2	Orange colour, with dolerite core-stone.	KwaZulu-Natal
18	BAUX3	Orange colour.	Australian bauxite
19	MD1	Orange colour, weathering profile, below 50 cm black soil.	Moorivier area <i>Farm:</i> Middeldraai
20	MD2	Orange colour, with dolerite core-stone.	
21	MD3	Orange colour, with dolerite core-stone.	
22	RYE1	Dark red nodular laterite	Ventersdorp area Ryedale ferromanganese open pit mine
Other samples			
23	SLV	Ochre to pale-brown nodules, dark-red to purple on fresh fractures.	Sri Lanka clay used in clay brick defluoridation systems
24	RBM	Processed bauxite, 100% amorphous Al ₂ O ₃ .	Australian bauxite obtained from Richards Bay Minerals
25	ALU	Activated aluminium.	Fluka, Type 504 C

groundwaters in South Africa (McCaffrey and Willis, 2001) are shown in Fig. 1(b). Table 1 lists the areas and the types of clay deposit sampled for this study. Samples were collected using a manual auger to a maximum depth of 2.5m. In many cases existing open pits allowed sampling at greater depths. In addition to samples collected in South Africa, clay samples obtained from Sri Lanka and Australia were included in the study for comparison.

Mineralogical characterisation of the clays

Sample preparation

A representative portion of each sample was dried overnight at 30°C, after visible pieces of plant material and pebbles were removed by hand. Each sample was lightly crushed in a swing-disk mill to an arbitrary chosen grain size of <180 µm. Each sample was then dispersed in distilled water using an ultrasonic bath. The clay fraction was separated by using standard centrifugal techniques (USGS, open file report 01-041). Decantation was not an acceptable alternative to centrifugation in this study because normal gravitational methods of particle sedimentation take an inordinate amount of time, and for particles <0.5µm in size Brownian motion interferes with settling (Folk, 1974; Syvitski, 1991). For each sample, three sedimented samples were prepared on glass slides and allowed to dry slowly to produce orientated deposits. One was heat-treated for 30 min at 550°C, one was left in a desiccator with ethylene glycol at 40°C for 24 h, and one was kept in a desiccator for X-ray diffraction.

Identification of clay minerals from X-ray diffraction

Step scans of 4 s per step of 0.05°2θ from 2.50°2θ to 16.00°2θ were done on air-dried, glycolated and heat-treated samples using a Phillips PW 1710 X-ray diffractometer with the following settings:

Tube anode material	Cobalt
Generator potential	40 kV
Wavelength Kα ₁	1.78896Å
Wavelength Kα ₂	1.79258Å
Intensity ratio I _{Kα1} /I _{Kα2}	2
Divergence diaphragm	1°
Detector diaphragm	0.1 mm

The changes in peak position on swelling and heating were used to confirm mineral identification (Velde, 1995). X-ray powder diffraction analyses were conducted on each sample using side-loaded aluminium sample holders to determine the overall mineralogical composition. These measurements were conducted in a step scan mode of 2 s per 0.04°2θ step, from 3.00°2θ to 80.00°2θ. Table 2 lists the results of semi-quantitative determination of the mineralogical composition of the selected clay samples.

Fluoride adsorption characteristics of the clays

Determination of adsorption capacity

Adsorption capacities for the different samples were determined at different pH values by shaking 1 g of washed and dried (2 h at 105°C) clay with 50 mL of 10 mgF·L⁻¹ NaF solution for 2 h in polyethylene bottles at 22°C. The initial pH was adjusted to between 3 and 9 using NaOH or HCl. The suspension was allowed to equilibrate for 12 h before adding 0.5 mL 1000 mgF·L⁻¹ NaF stock solution to 49.5 mL test solution using a micropipette. After equilibration the solutions were centrifuged, the pH measured to ensure that the pH was within +0.2 pH unit from the target pH, and the residual fluoride concentration determined using ion chromatography or a fluoride ion selective electrode. The % adsorption was calculated from the

residual fluoride concentration using the formula:

$$\% \text{ adsorption} = 100 \times (10 - [F]_{\text{residual}}) / 10.$$

To ensure that F⁻ does not adsorb onto the inner walls of the adsorption vessels, blank runs were performed. In this procedure a 10 mgF·L⁻¹ solution was added to a polyethylene vessel and the F⁻ concentration measured after 2 h and again after 12 h. No reduction in F⁻ concentration was found.

Pretreatment procedures

Heat treatment

In the heating pretreatment procedure, clays were placed in a preheated oven for 1 h at 600°C, cooled, and stored in desiccators: This procedure is denoted by the symbol C. To study the effect of heating clays at different temperatures, the same procedure was followed through the temperature range 200 to 800°C in steps of 100°C.

Pre-wash

Clays were checked for exchangeable fluoride that could be present in the material before adsorption measurements by extracting 1 g of clay with deionised water.

Chemical pretreatment

Clays were chemically activated by shaking with 0.1 M Na₂CO₃ for 30 min, washing with deionised water to remove excess carbonate followed by treatment with 1% HCl for 30 min and washing with deionised water until chloride-free. This procedure is denoted by the symbol CT.

Sequential pretreatment procedure

In the sequential treatment, samples were first heated for 1 h at 600°C and then treated chemically with Na₂CO₃ and HCl as above. This procedure is denoted by the symbol CTC.

Ammonium oxalate extraction

Selected clay samples were extracted with 0.2 M ammonium oxalate at pH 3 by shaking for 4 h in polyethylene bottles, filtered, washed with deionised water, and dried overnight at 105°C (Parfitt, 1989).

Results and discussion

Adsorption capacities of clay samples

The mineral composition and percentage F⁻ adsorbed from 10 mgF·L⁻¹ solutions at pH 6 are given in Table 2 for 25 clay samples selected from more than 50 collected from the northern parts of South Africa. The samples are grouped according to the major clay types identified in Table 1: bauxite, laterite, palygorskite, bentonite and kaolinite. Adsorption ranges from almost zero for certain kaolinites to up to 80% for a bauxitic clay of Australian origin and 99% for a processed bauxite consisting of amorphous Al₂O₃. Reproducibility was determined by three repeat measurements on selected samples. The standard deviation ranged from less than 10% for the bauxite samples to about 15% for the other sample types with lower adsorption capacities than the bauxites. For the processed bauxite (RBM) and activated alumina (ALU) where adsorption was close to 100% the reproducibility was better than 1%. The results show that high adsorption can be correlated with bauxitic and lateritic samples where the gibbsite and goethite/hematite contents are high. The lowest adsorption was found for kaolin samples.

TABLE 2											
Mineralogical composition of clay samples and % F⁻ adsorption at pH 6 from 10 mgF·ℓ⁻¹ solutions. xxxx: dominant(>50%); xxx: major (20-50%); xx: minor (5-20%); x: trace (<5%)											
Sample	% F ads	quartz	dolomite	kaolinite	palygorskite	mixed-layer clay	smectite	illite	talk	gibbsite	goethite/hematite
Bauxite (gibbsite/goethite)											
ALU	100									xxxx	
RBM	99									xxxx	
BAUX3	80	xxx								xxxx	x
BAUX1	65	xx								xxxx	xx
BAUX2	50	xx								xxxx	xx
MD1	68	xxx		xxx		x		xx		xx	xx
MD2	71	xxx				x				xxxx	xx
MD3	73	xxx				x				xxxx	xx
Laterite (goethite/hematite / kaolinite)											
SLV	72	xx		xxxx							xxx
RYE1	50	xxx		xx			x				xxx
PTA/LAT	40	xxx		xxx							xxx
LAT	23	xxx		xx		xxx		xx			
Palygorskite (dolomite/palygorskite)											
CAL	58	x	xxx		xxx		xxx				
DB1	43	xxx	xx		xxxx						
DB2	21	xx	xxxx		xxx						
LW1 ¹	23	xxxx			xxx	xx	xx				
Bentonite (smectite)											
NHM	45	xx		xx			xxxx				
BBK2	30	xxx					xxx				
BEN	20	xx					xxxx				
CF3	15	xxx					xxxx				
CF4	0	xx		x		xxx	xxx				
Kaolinite											
RNF	25	xxx		xxx			xxx	x	xx		x
ZEB1	5	xx		xxxx				x			
ZEB2	4	xx		xxxx					xx		
ZEB6	6	xx		xxxx		xx	xx	x			
(1) Also contains feldspar (xxx)											

Table 3 gives the idealised chemical composition of the major mineral types found in the clays investigated in the order in which they were found to adsorb fluoride from aqueous solutions. Adsorption capacities were estimated from adsorption data at pH 6 and initial fluoride concentrations of 10 mgF·ℓ⁻¹.

In Table 4, published adsorption capacity data for different soil and clay types are compared with the values obtained in this study. Data estimated for an initial F⁻ concentration of about 10 mg·ℓ⁻¹ and

pH between 5 and 7 are included. The comparison gives an approximate indication of fluoride adsorption trends for a wide variety of soils and clays from all over the world although the numerical adsorption values are not exactly comparable because experimental conditions differed. These results support the conclusion that hydrated aluminium oxide and iron oxide surfaces occurring in bauxites and goethites/hematites are useful substrates for fluoride adsorption.

Clay type	Idealised chemical composition	F adsorption capacity mg·g ⁻¹	Fluoride adsorption
gibbsite	Al(OH) ₃	0.25 - 0.4	high
goethite	FeO.OH	0.2 - 0.3	high
palygorskite	(Mg,Al)Si ₈ O ₂₀ (OH) ₂ ·8H ₂ O	0.1 - 0.3	intermediate
smectite	Ca(Mg,Fe)(Si,Al) ₄ O ₁₀ (OH) ₂ ·nH ₂ O	0.1 - 0.2	low intermediate
kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	< 0.05	low

Sorbent type	Sample name and description	Adsorption capacity mg·g ⁻¹	Reference
Bauxite			
activated alumina	Type 504C, Fluka	0.5	This work
gibbsite	BAUX3 Australia BAUX1, BAUX2 South Africa	0.40.25 - 0.4	This work This work
Goethite			
goethite/kaolinite	PTA-LAT South Africa	0.2	This work
goethite/illite	Tertiary soil Shanxi China	0.23	Wang and Reardon, 2001
goethite / kaolinite	SLV Sri Lanka	0.35	This work
Palygorskite			
palygorskite /dolomite	DB1, CAL South Africa	0.21– 0.29	This work
Bentonite			
smectite	BEN South Africa	0.1	This work
	Bentonite Wyoming, USA	trace	Bower and Hatcher, 1967
	Alkaline soils USA	0.04–0.08	Bower and Hatcher, 1967
Kaolinite			
kaolinite	ZEB6 South Africa	0.03	This work
	Acid soils USA	0.17–0.25	Bower and Hatcher, 1967
	Acid soils Illinois, USA	0.13	Omuetti and Jones, 1977
	Potter's clay, 30% Al ₂ O ₃ 1106 White St Thomās	0.12	Bårdsen and Bjorvatn, 1995
	Clay pots Ethiopia	0.07	Moges et al., 1996

The pH dependence of the adsorption process is illustrated in Fig. 2 for a few mineral types. Data for H-151 and GOETH were taken from the literature (Hao et al. (1986). H-151 is a commercial activated alumina type and GOETH is a goethite sample. Typically the adsorption is low at pH values <3 and >8. Maximum adsorp-

tions are achieved at pH 5 for aluminium oxide type sorbents and pH 3.5 for iron oxide types such as goethite.

Clearly the adsorption capacity is determined by the structure of the clay and in particular the surface charge distribution as a function of pH. The adsorption capacity seems to increase with

increasing Al and Fe oxide content. Thus, the more basic the surface and the more easily it can be protonated at pH values above 3 the better are the adsorption characteristics of the clay. At pH values below 3 fluoride is completely protonated to form neutral HF and therefore rapidly loses its ability to adsorb onto positive surfaces. The discussion of the mechanism (Hao et al., 1986) of adsorption in relation to the mineral structure, is beyond the scope of this paper.

Effect of chemical and physical pretreatment procedures

A few of the clay types that showed above average fluoride adsorption tendencies were selected to determine the effect of chemical and physical treatment on the possible enhancement of adsorption capacity. The selected clay types were: gibbsite-goethite (MD2), palygorskite-dolomite (CAL), kaolinite-goethite (SLV), and amorphous Al_2O_3 (RBM). Activated alumina (ALU) was included for comparison.

For clay sample MD2, consisting mainly of gibbsite and a minor amount of goethite, a slight increase in adsorption capacity was observed with increasing heat treatment temperature up to 600°C followed by a decrease at temperatures above 600°C as shown in Fig. 3. Similar results can be found in the literature (Hauge et al., 1994) for clays with high concentrations of Al oxides. The decline in adsorption capacity above 600°C can be attributed to the gradual conversion of gibbsite into $\alpha-Al_2O_3$ that has a lesser tendency to adsorb fluoride.

In the case of goethites a similar reduction in adsorption capacities after heat treatment at temperatures above 600°C was observed (Wang and Reardon, 2001). This may be attributed to the formation of magnetites, a form of iron oxide which shows little tendency to adsorb fluoride. The temperature of 600°C therefore represents an upper limit above which F^- adsorption decreases for the clay types containing Al and Fe oxides. Should clays be used as substrates for F^- removal, lower temperatures could be used without significantly changing adsorption capacities.

The dolomite in samples such as CAL can also play a role in F^- adsorption. It was found that adsorption increased after these clays were heated to 600°C. This could be attributed to the conversion of calcium and magnesium carbonates into oxides of these metals. Subsequent exposure of the freshly formed CaO to F^- could result in the formation of CaF_2 . This process could contribute to F^- removal from the solution through a precipitation mechanism rather than an adsorption or ion exchange mechanism.

Figure 4 summarises the effect of heat treatment and chemical treatment on the adsorption capacities of the selected clay types. Chemical treatment had a significant effect on the adsorption capacities of certain clays such as palygorskite-dolomite (CAL), kaolinite-goethite (SLV), and amorphous Al_2O_3 (RBM), but little change was observed for gibbsite-goethite clay (MD2). Activated alumina was included as a reference. The pretreatment procedures were not expected to affect the adsorption characteristics of this sorbent.

To assess the contribution of amorphous components to the overall F^- adsorption capacity of clays, an ammonium oxalate extraction was performed. The F^- adsorption capacity was determined before and after the extraction. The clays MD2 and SLV contain gibbsite and goethite and are therefore likely to also have substantial amounts of amorphous aluminium and iron oxides as a result of weathering. The results show a drop of ca. 70% in the adsorption capacity for MD2 at pH6 and a drop of ca. 80% for SLV after extraction. This would indicate that amorphous Al and Fe oxides play a very important role in the adsorption capacities of the

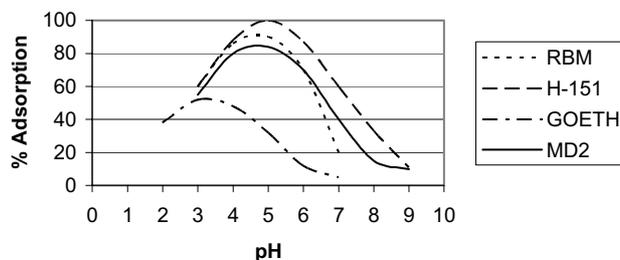


Figure 2

pH dependence of fluoride adsorption for different mineral sorbents:

RBM = amorphous Al_2O_3 ; H-151 = activated alumina type H-151; GOETH = goethite; MD2 = gibbsite/goethite

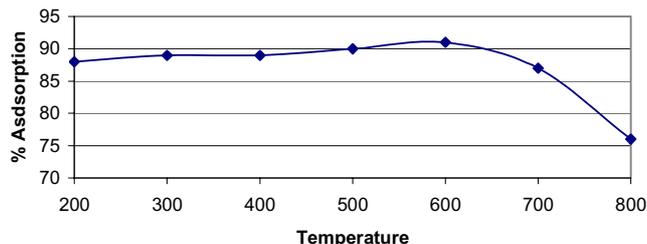


Figure 3

Percentage adsorption for the bauxitic clay (MD2) as a function of heat treatment temperature

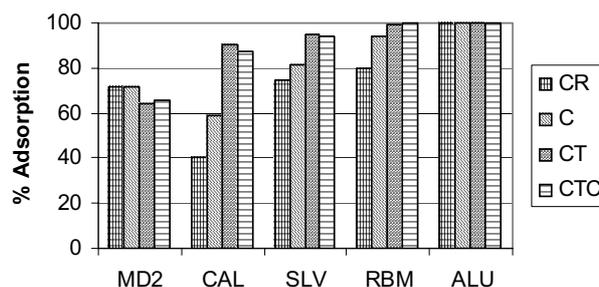


Figure 4

Effect of heating and chemical treatment on adsorption capacities of selected samples. CR = clean raw, C = heated for 1 h at 600°C, CT = chemically treated with 1% Na_2CO_3 and 1% HCl, CTC = heated and followed by chemical treatment

clays. The ammonium oxalate method is used to dissolve by complexation Al and Fe from amorphous phases in clays and soils (Parfitt, 1989).

Conclusions

From this study the following conclusions may be drawn:

- Not many South African clays were found to be useful as adsorbents for F.
- Clays consisting of substantial amounts of gibbsite or aluminium oxides have shown the best overall potential as fluoride adsorbents.
- Chemical treatment of the clay substrates with Na_2CO_3 and HCl solutions and heat treatment to <600°C can improve the adsorption capacities of some clays.

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