



# Inhibition of the formation and stability of inorganic colloids in the alkaline disturbed zone of a cementitious repository

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## ABSTRACT

The generation and stability of inorganic colloids have been studied under hyperalkaline conditions. For the generation of colloids, intact cores of Bromsgrove Sandstone were flushed with simulated cement leachates, and the eluates were ultrafiltered sequentially (12  $\mu\text{m}$ , 1  $\mu\text{m}$ , 0.1  $\mu\text{m}$  and 30 kDa) for the separation of any colloids found. No colloid formation was observed during the experiments; however the analysis by ICP-MS of the eluates showed significant increases in Si and Al, indicating silicate mineral dissolution, as well as reduction of the concentration of Ca in the leachates indicating precipitation of secondary Ca-rich phases. Flow experiments with cement leachates spiked with tritiated water showed a noticeable reduction of the porosity of the sandstone as well as changes in the pore distribution. Additional stability experiments were carried out using model silica and  $\text{Fe}_2\text{O}_3$  colloids. The experiments indicated that the stability of the colloids was mainly controlled by the concentration of Ca in solution and that both types were unstable under the chemical conditions in the alkaline disturbed zone. The presence of cement additives such as superplasticisers could enhance the stability of the colloids.

**KEYWORDS:** colloids, alkaline disturbed zone, silica, iron oxide.

## Introduction

THE current concept for the disposal of intermediate- and low-level waste in the UK involves the placement of grouted waste confined in steel canisters in a deep geological disposal facility (GDF). After closure, the mined vaults in the GDF will be backfilled with cementitious material that will contribute to the containment of radionuclides by a combination of chemical processes, namely solubility limitation, precipitation, co-precipitation and sorption (Nuclear Decommissioning Authority, 2010). While the cement will buffer the pore water

to a highly alkaline pH, this could potentially create an alkaline plume penetrating from the repository into the host rock, perturbing the chemistry within a zone referred to as alkaline disturbed zone (ADZ). The alkaline cement leachate can react with the host rock, promoting dissolution of some mineral phases, precipitation of new phases (Daizères *et al.*, 2010) and the generation of colloids (Mashal *et al.*, 2004) that may affect radionuclide movement within the chemically disturbed zone of the host rock. The nature, stability and mobility of the colloids in the ADZ have been identified as sources of uncertainty in the performance assessment of a cementitious GDF (Swanton *et al.*, 2009).

Swanton *et al.* (2009) carried out a review of the generation and behaviour of colloids under near-field conditions; the authors concluded that in the

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presence of low concentrations of organic compounds the stability of the colloids would depend mainly on the ionic strength, and the high concentration of calcium in the pore water is expected to cause the destabilization of the colloidal particles. Although the cementitious colloids are thermodynamically unstable under low pH conditions, there is a lack of experimental evidence of their behaviour under ADZ conditions (Swanton *et al.*, 2009, and references therein). Wetton *et al.* (1998) investigated the generation of colloids at Maqarin (Jordan), a natural analogue site, looking at the silica colloid production at the cement/host rock interface; from the small amount of material collected the authors suggested that the colloids in the interface had their origin in the cement zone. Another conclusion was that there were significant differences between the population and characteristics of the colloids found under laboratory conditions and those found at the natural analogue site. Several studies have investigated the formation of colloids from sediments in contact with the alkaline leachates from underground storage tanks in the Hanford Reservation (USA) in batch and column experiments (Flury *et al.*, 2002; Mashal *et al.*, 2004). Under flow conditions Flury *et al.* (2002) only observed significant mobilization of colloids when the ionic strength of the eluents was reduced from 1 to  $10^{-3}$  mol dm<sup>-3</sup>.

The aim of the present work is to study the generation of inorganic colloids from a generic host rock and the chemical changes induced in it by the advection of an alkaline plume through an intact

rock core. Colloids can potentially increase the effective mobility of radionuclides, hence the importance of the study of colloid stability under ADZ conditions. The effects on colloid stability of diverse aspects of the chemistry of the cement leachates such as pH and Ca concentration will be assessed. Additionally, the effect of the presence of natural organic matter (humic acid), cement additives (superplasticisers) and cellulose degradation products from the waste packages will be also studied, as the presence of organics may increase the stability of colloids and therefore enhance their transport (Degueudre *et al.*, 2000).

## Experimental

### Testing colloid generation in intact sandstone under flow conditions

For the study of colloid generation under the conditions of an alkaline disturbed zone (ADZ) a series of flow experiments were set up in which an intact core of sandstone was put into contact with a synthetic young cement leachate under dynamic conditions. The sandstone selected for this study was from the Bromsgrove Sandstone Formation of the Sherwood Sandstone Group (Hollington Sandstone Quarry, Hollington, Uttoxeter, Staffordshire). It was chosen as 'generic' quartzo-feldspathic rock with sufficient permeability to enable the laboratory flow experiments to be carried out on intact material. Intact rock with natural 'groundwater-aged' mineral surfaces was preferred so as to avoid the experiments being influenced by reaction with fresh mineral surfaces, which would be the case if columns of crushed rock had been used. The main mineral components of this sandstone appear in Table 1.

The sandstone cores had 50 mm diameter and 100 mm length and the sides were coated with an impermeable epoxy resin so that the cement leachate could only pass through the ends. In order to reduce preferential flow paths, the solution was injected upwards into the sandstone cores, against gravity. A similar experimental set-up has been reported by Bryan *et al.* (2005). Two types of experiment were carried out; (i) intermittent contact of the cement leachates with the sandstone and (ii) continuous contact of the cement leachates with the rock at constant rate. The set-up for the first type of experiments has been adapted from the filtration rig used by Warwick *et al.* (2002). The cement leachate is contained in a reservoir under an N<sub>2</sub>-atmosphere and the pressure of N<sub>2</sub> drives the solution from the

TABLE 1. The main mineral components of the Bromsgrove Sandstone.

Mineral component	Volume %*
Quartz	76
K feldspar	16
Illite/chlorite/smectite	4
Kaolinite	3
Muscovite	1

\*Normalized after excluding porosity.

Trace amounts (<1%) of albite, hematite, TiO<sub>2</sub>, zircon, biotite (or other Fe mica) and apatite were identified by detailed petrographic analysis but are below the level for SEM-EDX quantification.

No carbonate minerals (calcite, dolomite) were observed to be present in the sandstone.

container into the sandstone core and into the filtration rig for sequential ultrafiltration and removal of the colloidal particles. In this experiment the sandstone was intermittently in contact with the cement leachate over periods of 7–8 hours, followed by stop-flow periods of 17–16 hours, during which filtration occurred. In the second type of experiment, the intact core of sandstone was pumped at constant flow ( $50 \text{ cm}^3 \text{ h}^{-1}$ ) with a peristaltic pump inside a glove box under nitrogen atmosphere, and fractions of  $2.5 \text{ dm}^3$  were collected in a reservoir and then sequentially filtrated. Four different sized membranes were used,  $12 \mu\text{m}$  (Whatman polycarbonate Cyclopore),  $1 \mu\text{m}$  (Whatman polycarbonate Nuclepore),  $0.1 \mu\text{m}$  and  $30 \text{ kDa}$  (Amicon YM cellulose). After filtration, the excess of alkali solution was removed by applying a flow of  $\text{N}_2$  through the filtration rig for 1h; washing of the filters with deionized water was avoided since the changes in the composition or pH could potentially cause the re-dissolution of any of the collected colloids. The membranes were dried and kept in a glove-box in a  $\text{N}_2$ -atmosphere before imaging of the surface by scanning electron microscopy (SEM). Phase identification under the SEM was based on qualitative chemical information obtained by energy-dispersive X-ray microanalysis (EDX) recorded simultaneously during SEM observation.

Throughout the experiments, aliquots of the leachate were sampled at the outlet of the sandstone cores and the main components of the solution were analysed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent, 7700x Series, Stockport, UK) in semi-quantification mode before and after filtration with Whatman VecatSpin centrifuge filter tubes ( $30 \text{ kDa}$  MWCO, polysulphone membrane). All samples, pre- and post-ultrafiltration, were acidified with  $\text{HNO}_3$  (TraceSELECT@Ultra from Fluka, Steinheim, Germany) before their analysis by ICP-MS. The changes in porosity caused by the flow of the alkaline fluid through the stone were also monitored by observation of the breakthrough curves of tritiated water (HTO, Perkin Elmer) through the core. For this purpose, the cement leachates were spiked with HTO ( $20 \text{ Bq cm}^{-3}$ ) and pumped with a peristaltic pump at constant flow ( $50 \mu\text{l min}^{-1}$ ) through the rock;  $1\text{--}1.5 \text{ cm}^3$  aliquots were sampled with a fraction collector (Frac-920, GE Healthcare, Uppsala, Sweden) and mixed with  $10 \text{ cm}^3$  liquid scintillation cocktail (Gold Star Multipurpose Liquid scintillation cocktail, Meridian, Epsom, Surrey, UK) before measurement in the energy

range between 0 and  $18.6 \text{ kV}$  (TRI-CARB 2500 TR Liquid Scintillation Counter, Packard).

### Stability of synthetic colloids

The stability of colloids under the conditions of an ADZ was assessed in batch experiments using two model colloidal materials; silica (LUDOX® TM-50 colloidal silica, Aldrich, Steinheim, Germany) and  $\text{Fe}_2\text{O}_3$  nanoparticles ( $100 \text{ nm}$  DLC particle size, Aldrich, Steinheim, Germany).  $\text{Fe}_2\text{O}_3$  nanoparticles have been selected as a model of Fe colloids, as previous work regarding long-term rock alteration under ADZ conditions showed no evidence of the reduction of hematite (Moyce *et al.*, 2014). In all the experiments, the colloid concentrations were  $0.5 \text{ wt.}\%$  and  $0.2 \text{ wt.}\%$  for silica and  $\text{Fe}_2\text{O}_3$ , respectively. Three series of experiments were carried out for both silica and  $\text{Fe}_2\text{O}_3$  to assess the effect of pH, in which increasing concentrations of either NaOH (laboratory reagent grade,  $>98\%$ , Fisher Scientific) or KOH (analytical reagent grade, Fisher Scientific, Loughborough, UK) were added to the colloids suspensions in  $0.01 \text{ mol dm}^{-3}$   $\text{NaClO}_4$  ( $98\%$  extra pure, Acros Organics, Geel, Belgium) in the range between  $10^{-6}$  and  $10^{-1} \text{ mol dm}^{-3}$  or  $\text{Ca(OH)}_2$  (laboratory reagent grade, Fisher Scientific, Loughborough, UK) between  $10^{-6}$  and  $10^{-2} \text{ mol dm}^{-3}$ .

The effect of the concentration of calcium on the stability of the colloids was determined by the addition of Ca in the range between  $10^{-7}$  and  $10^{-2} \text{ mol dm}^{-3}$  as  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , for analysis, Fisher Scientific, Loughborough, UK) at pH 13 ( $0.05 \text{ mol dm}^{-3}$  NaOH +  $0.05 \text{ mol dm}^{-3}$  KOH). In order to mimic conditions such as intrusion of cement leachates in the host rock of the repository, experiments were performed in which increasing proportions of either young (YCL) or intermediate cement leachate (ICL) (see compositions in Table 2) were mixed with the suspensions of silica or  $\text{Fe}_2\text{O}_3$  in  $0.01 \text{ mol dm}^{-3}$   $\text{NaClO}_4$ . The presence of organic compounds can also influence the stability of colloids; the organics could be already present in the host rock for example as humic acid (HA) and they could be carried by the alkaline plume, such would be the case of cement additives (superplasticisers) or be the result of the alkaline degradation of the cellulose in the intermediate and low-level waste (cellulose degradation products, CDP).

Thus, all the experiments were repeated in the absence of organic compounds as well as in either  $5 \text{ ppm}$  of HA,  $0.5\%$  (w/w) superplasticiser or  $10^{-3} \text{ mol dm}^{-3}$  isosaccharinic acid (ISA, main

TABLE 2. Composition of the artificial cement leachates.

Young cement leachate (YCL)	Intermediate cement leachate (ICL)
5.2 g dm <sup>-3</sup> KOH	0.296 g dm <sup>-3</sup> KCl
3.8 g dm <sup>-3</sup> NaOH	10 mg dm <sup>-3</sup> NaCl
0.1 g dm <sup>-3</sup> Ca(OH) <sub>2</sub>	1.2 g dm <sup>-3</sup> Ca(OH) <sub>2</sub>
11.4 mg dm <sup>-3</sup> NaHCO <sub>3</sub>	0.37 mg dm <sup>-3</sup> MgCl <sub>2</sub>
pH 13.1	0.5 mg dm <sup>-3</sup> Na <sub>2</sub> CO <sub>3</sub>
	pH 12.3

component of the CDP). Before use, the HA (Aldrich, Steinheim, Germany) had been purified following the procedure described by Kim *et al.* (1991). The sodium salt of ISA was produced in-house by the synthesis procedure reported by Whistler and Be Miller (1963). ADVA<sup>®</sup> Cast 550 (Grace Construction products) was the cement additive selected as model of the behaviour of comb-type polycarboxylate superplasticisers. The stability of the colloid particles was assessed by means of the changes of intensity of the dynamic light scattering (DLS) signal as well as electrophoretic light scattering (ELS) (Zetamaster, Malvern Instrument Ltd, UK). DLS measurements were validated daily by the analysis of a Nanosphere<sup>™</sup> size standard (polystyrene polymer, 216 ± 4 nm, Thermo Scientific). Samples were measured in polystyrene disposable cuvettes (Fisherbrand<sup>™</sup>, Fisher Scientific) at an angle of 90° to the incident beam (670 nm) and the multimodal method was used for the analysis of the correlograms. A zeta potential transfer standard (50 ± 5 mV, Malvern Instrument Ltd, UK) was used for validation of ELS data. Single-factor ANOVA indicated that there were no significant differences ( $F = 2.2186 < F_{\text{critical}} = 2.6645$ ) between the blank values with and without organic compounds; therefore the presence of a colloidal organic fraction in the liquid media could be discarded. All experiments were carried out in triplicate. Initial kinetic studies between 1 and 100 hours after the addition of the reagents to the colloidal suspensions indicated that no further changes in the stability of the colloids were observed after 18 hours; therefore all the results presented in the later section on the stability of synthetic colloids correspond to 18 hours. At the end of the equilibration time, pH values were also measured for all the suspensions using a semi-micro pH electrode provided by Fisher Scientific (Loughborough, UK) calibrated on a

daily basis with buffers at pH 7.00 (phosphate buffer), 10.01 (carbonate/bicarbonate) both provided by Thermo Scientific (The Netherlands) and pH 13.00 (Reagecon, Ireland).

## Results and discussion

### Sandstone alteration under flow conditions

#### Generation of colloids and porosity changes

Of the six cores of sandstone treated with cement leachates under flow conditions, three of them blocked completely, and for the other three breakthrough and elution profiles of HTO could be obtained before and after the treatment with the alkaline solution. Initially the breakthrough of HTO occurs after the injection of ~24 cm<sup>3</sup> of spiked leachate, which would correspond to a volumetric porosity of 12%. After treatment with YCL (approx. 12.5 dm<sup>3</sup>) the breakthrough of HTO happens after the injection of only 8 cm<sup>3</sup>, which corresponds to a reduction of the overall porosity down to 4%. After treatment with YCL the injection profile is more gradual, and it shows two slopes, which could indicate first rapid flow through preferential channels causing fast breakthrough of HTO and then slower flow into smaller pores. Petrographic analysis of the sandstone cores showed the localized formation of fine microporous secondary C(K)SH reaction products choking the primary intergranular porosity of the sandstone near the injection inlet of the core.

A total of 36 filters were observed by SEM and particles could only be found on the 12 µm filters corresponding to the first fractions of YCL through the sandstone (between 2 and 2.5 dm<sup>3</sup> YCL through the core). The EDX analyses of these particles indicate the presence of significant amounts of Si and Al. No Fe traces could be found in any of the particles analysed. However, further along the duration of the experiments (up to 10–12.5 dm<sup>3</sup> YCL were passed through the cores) no other Si/Al particles could be found in any of the filters. This would suggest that these particles are formed not by chemical reaction of the YCL with the sandstone by dissolution and precipitation, but they may be due to physical dislocation or disaggregation of the finer particles within the sandstone. Similar results were obtained for both types of experiments under intermittent contact or constant flow. Few smaller particles could be observed on the 0.1 µm and 30 kDa filters, which presented very high concentrations of Na and Ca. However, these particles were discounted as real

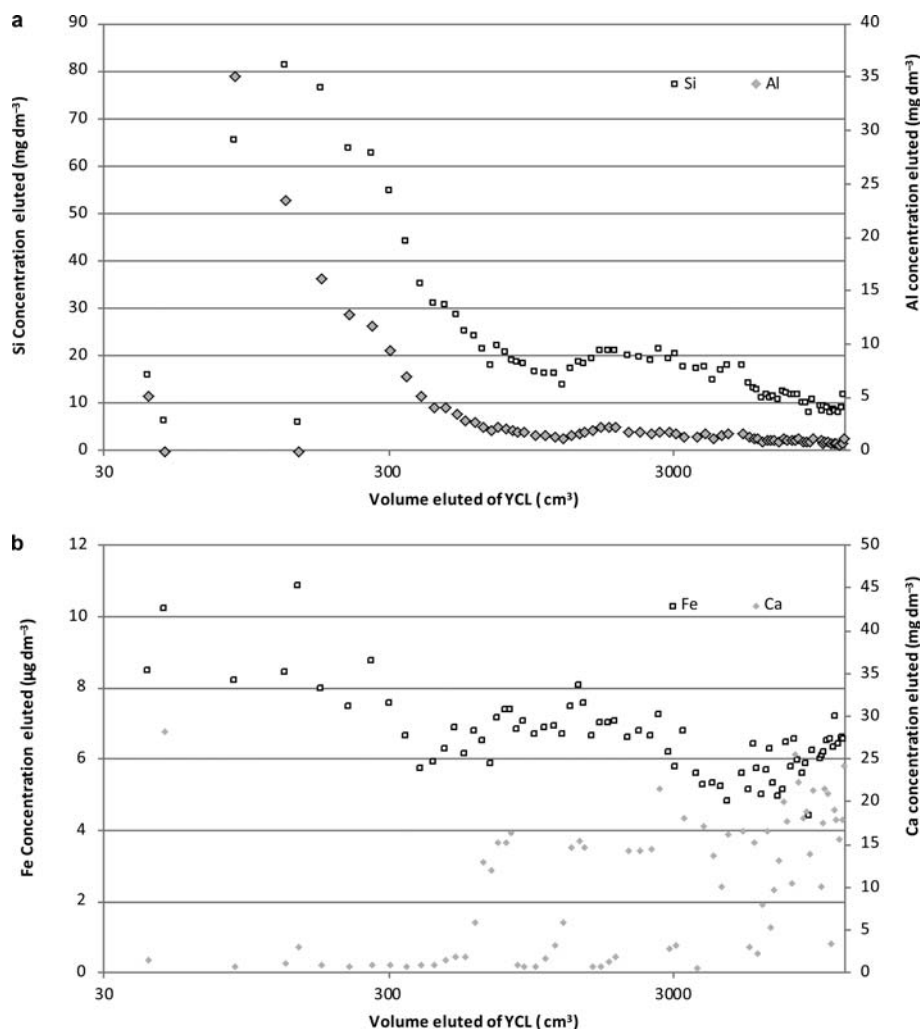


Fig. 1. Metal concentrations in the young cement leachate at the outlet of the intact sandstone cores (a) Si and Al and (b) Ca and Fe.

colloids formed by reaction with the sandstone, but they were considered to be artefacts resulting from the crystallization on the filters of traces of the YCL components. Therefore, it was concluded that under these experimental set-ups either no colloids were generated as result of the contact of YCL with intact sandstone under dynamic conditions, or colloids were formed but the chemical composition of YCL caused their precipitation within the sandstone fabric. To assess the latter hypothesis, batch studies with synthetic silica and  $\text{Fe}_2\text{O}_3$  colloids were carried out (see results in the section on stability of synthetic colloids).

#### *Sandstone dissolution*

In addition to potential formation of colloids, the flow of cement leachates can induce the solubilization of some of the mineral components in the sandstone. Therefore, aliquots of the leachate at the outlet of the cores were analysed by ICP-MS in semi-quantitative mode. Figure 1a shows the elution profiles of Si and Al in YCL, and as can be observed, both elements showed similar trends, with a sharp increase of the concentration within the first 100 cm<sup>3</sup> of YCL through the core, reaching the maximum concentration (up to 35 and 80 mg dm<sup>-3</sup> for Al and Si, respectively) after

$\sim 150 \text{ cm}^3$  (around 6 pore volumes), followed by a gradual decrease of the concentrations and finally reaching stable values after  $600 \text{ cm}^3$  (25 pore volumes). The concentration of Al and Si detected by ICP-MS was similar for the samples pre- and post-ultrafiltration with 30 kDa membranes; therefore it can be concluded that these two elements are present in solution in the eluted cement leachates and not as colloidal particles.

Other elements show similar trends to the one observed for Al and Si, with most trace metals such as Sr, W, Sn, Pb, Sb, Ni, V, Co, Cr and Cu in the range of  $\mu\text{g dm}^{-3}$ , showing a sharp peak between 100 and 200  $\text{cm}^3$  of YCL through the core. A few elements such as Ba and Ga showed a slow increase of the concentration in solution, up to  $0.6 \text{ mg dm}^{-3}$  and  $20 \mu\text{g dm}^{-3}$  for Ba and Ga respectively, reaching stable values after  $6000 \text{ cm}^3$  of YCL.

Figure 1b shows that there was very little dissolution of Fe, and it was only detected in the eluted YCL at trace levels, between 5 and  $12 \mu\text{g dm}^{-3}$ . As for the other metals, Fe reached its maximum concentration in solution within the first 4 and 8 pore volumes, however, it did not show the sharp peak observed for Al and Si.

The concentration of Ca in YCL (see composition in Table 2) is  $54 \text{ mg dm}^{-3}$ , and as can be observed, the concentration in the eluted YCL was 50% or below the value at the inlet, in some cases below  $1 \text{ mg dm}^{-3}$ , especially at the beginning of the experiment and it never reached its maximum concentration (Fig. 1b), despite the fact that the concentrations for the other elements had reached a steady state. Similar behaviour was observed in the flow experiments through Clashach sandstone carried out by Braney *et al.* (1993), where they observed retention of 24% (or higher) of the concentration of Ca at the inlet. Ramsay *et al.* (1991) performed leaching experiments using discs of OPC and St Bees sandstone under batch conditions, observing not only dissolution of Al and Si but also the deposition on the sandstone of Ca-rich particles. Therefore, despite the lack of colloids in the eluted YCL, these concentration profiles clearly show how the YCL causes dissolution of some of the mineral components of the sandstone on one hand, and on the other hand, the reduction in the concentration of Ca in the YCL could suggest precipitation of new mineral phases. The variation profiles observed in the present work for Si and Ca could be explained by the two-phase mechanism suggested by Usui *et al.* (2006), in which at the initial stage the silica particles offer a high surface area resulting in concentrations of

dissolved Si higher than Ca, and therefore all the Ca is removed from the leachate as CSH gel. As precipitation continues the surface area accessible for Si dissolution decreases, reducing the amount of silica in solution and the excess Ca elutes from the rock. In the present work, petrographic analysis of the sandstone cores showed the precipitation of fine CSH gel or microfibrils CSH locally within the pore network, which could account for the decrease in Si and Ca in solution.

### Stability of synthetic colloids

The stability of colloids in ADZ is likely to be affected by the chemistry of the cement leachate; therefore in the present work the effects of pH and the concentration of Ca were studied. When assessing the effect of the pH on the stability of the colloids, it must be noted that due to the concentration of the background electrolyte ( $0.01 \text{ mol dm}^{-3} \text{ NaClO}_4$ ), the addition of concentrations of either NaOH, KOH or  $\text{Ca(OH)}_2$  of  $10^{-3} \text{ mol dm}^{-3}$  or higher (i.e.  $\text{pH} \geq 11$ ) causes a variation not only in the pH but also in the ionic strength of the solutions; therefore the changes in the stability of the colloids cannot be attributed unequivocally to the pH, but they might be the result of the combination of pH and ionic strength increases. The values shown in the figures in this section correspond to average  $\pm \text{SD}$  of three replicates.

### Effect of pH

Figures 2 and 3 present the effect of NaOH and  $\text{Ca(OH)}_2$  on silica and  $\text{Fe}_2\text{O}_3$  colloids, respectively, and show that in general terms  $\text{Fe}_2\text{O}_3$  colloids are more sensitive to changes in pH than silica. The light scattering data showed (Fig. 2a) precipitation of the silica colloids at concentrations of NaOH around  $10^{-2} \text{ mol dm}^{-3}$  and pH values between 10 and 11, while  $\text{Fe}_2\text{O}_3$  seemed more affected by the presence of NaOH, with noticeable reduction of the number of particles in solution from pH 7 in  $10^{-3} \text{ mol dm}^{-3}$  NaOH (Fig. 3a); this point corresponded with a clear change on the surface charge of the  $\text{Fe}_2\text{O}_3$  colloids from positive to negative, as shown by the Zeta potential data in Fig. 3b. Puls and Powell (1992) also reported a change in the sign of the surface charge of 100–300 nm  $\text{Fe}_2\text{O}_3$  colloids in  $\text{NaClO}_4$  media between pH 6 and 7.

Moreover, there were no significant differences between the behaviour of silica in the presence and in the absence of organic compounds with increasing amounts of NaOH, while for  $\text{Fe}_2\text{O}_3$  the presence of 0.5% ADVA<sup>®</sup> Cast 550 stabilized the

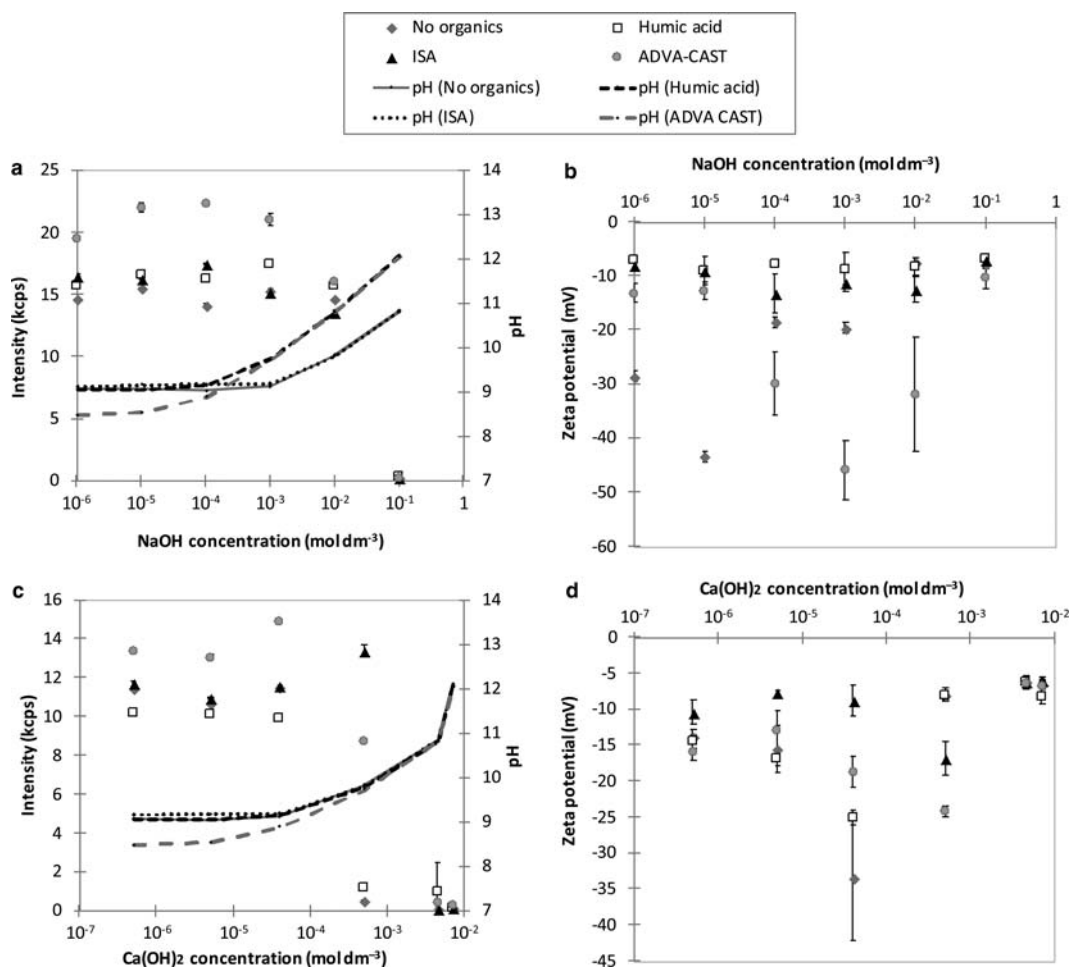


Fig. 2. Light scattering intensity and Zeta potential as a function of the pH for silica colloids in the presence of NaOH (a) light scattering and (b) Zeta potential and in the presence of  $\text{Ca}(\text{OH})_2$  (c) light scattering and (d) Zeta potential.

colloids up to pH 12. The Zeta potential data would suggest that the superplasticizer adsorb to the  $\text{Fe}_2\text{O}_3$  colloids, making the charge on the surface of the colloids almost neutral; the addition of NaOH changes the Zeta potential to negative values; however this change was much more dramatic with no organics or with HA or ISA, than with ADVA<sup>®</sup> Cast 550.

When comparing the effect of NaOH (Fig. 2a) and  $\text{Ca}(\text{OH})_2$  (Fig. 2c) on silica, it can be observed that the presence of  $\text{Ca}(\text{OH})_2$  has a bigger destabilizing effect than NaOH, and precipitation is observed from concentrations of  $\text{Ca}(\text{OH})_2$  around  $10^{-3} \text{ mol dm}^{-3}$ , the same value as the one reported by Ramsay *et al.* (1991). The Zeta potential data for

silica did not offer a clear picture of the effect of NaOH and  $\text{Ca}(\text{OH})_2$  on silica colloids stability; in the presence of HA and ISA there was little variation of the Zeta potential, between  $-15$  and  $-5 \text{ mV}$ , while in the other cases the oscillation of the potential was stronger, going down to  $-35$  or  $-45 \text{ mV}$ . Ramsay *et al.* (1991) attributed the destabilization effect of  $\text{Ca}(\text{OH})_2$  due to the sorption of  $\text{Ca}^{2+}$  ions to the silica surfaces, causing neutralization of the charge. However, in the present work, the Zeta potential measurements did not clearly support this hypothesis; furthermore, the oscillations of the Zeta potential values in the presence of  $\text{Ca}^{2+}$  and non-complexing ions ( $\text{Na}^+$  and  $\text{K}^+$ ) were similar. An alternative

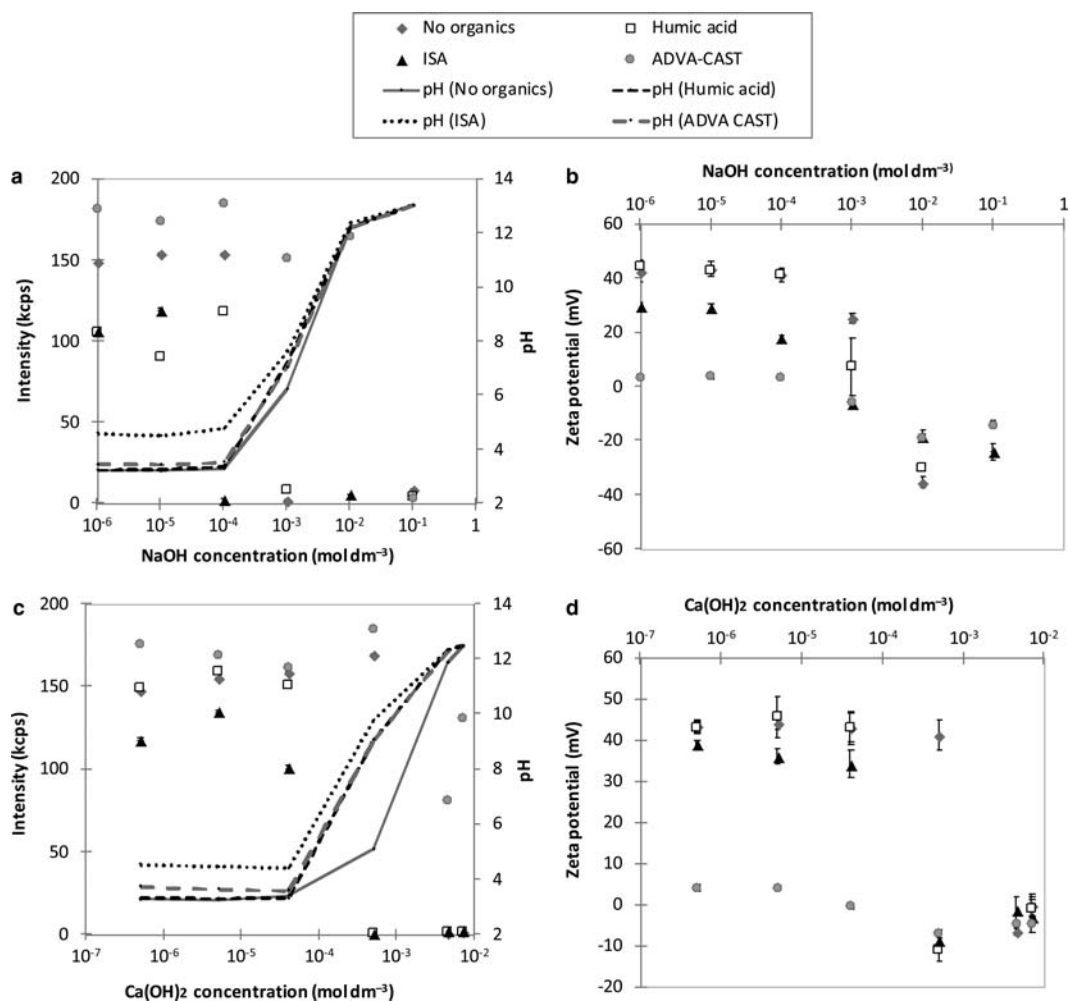


FIG. 3. Light scattering intensity and Zeta potential as a function of the pH for  $\text{Fe}_2\text{O}_3$  colloids in the presence of NaOH (a) light scattering and (b) Zeta potential and in the presence of  $\text{Ca}(\text{OH})_2$  (c) light scattering and (d) Zeta potential.

explanation of the effect of  $\text{Ca}(\text{OH})_2$  would be the contraction of the electrical double layer of the negatively charged silica colloids (Ramsay, 1986; Ramsay *et al.*, 1991), of which  $\text{Ca}^{2+}$  acts as counter ion.

Regarding  $\text{Fe}_2\text{O}_3$ ,  $\text{Ca}(\text{OH})_2$  caused precipitation of the colloids at a concentration around  $5 \times 10^{-4} \text{ mol dm}^{-3}$  (Fig. 3c), a lower concentration than for NaOH, which corresponded to a sharp change in the Zeta potential from +50 mV to negative values between -10 and -2 mV (Fig. 3d). This fits with the observations by Liang and Morgan (1990), who concluded that Ca is more effective than Na as a coagulant of  $\text{Fe}_2\text{O}_3$  particles as can be qualitatively predicted by the Schulze-

Hardy rule (Nowicki and Nowicka, 1994). ADVA<sup>®</sup> Cast 550 stabilized the  $\text{Fe}_2\text{O}_3$  colloids to higher concentrations of  $\text{Ca}(\text{OH})_2$ , keeping the Zeta potential of the colloids around neutral values. The addition of increasing concentrations of KOH between  $10^{-6}$  and  $10^{-1} \text{ mol dm}^{-3}$  had a similar effect to the one observed in the presence of NaOH for both silica and  $\text{Fe}_2\text{O}_3$ .

#### Effect of Ca concentration at pH 13

Another aspect of the composition of the alkaline plume is the concentration of Ca; therefore increasing concentrations of Ca (as  $\text{Ca}(\text{NO}_3)_2$ ) in the range between  $10^{-7}$  and  $10^{-2} \text{ mol dm}^{-3}$  were



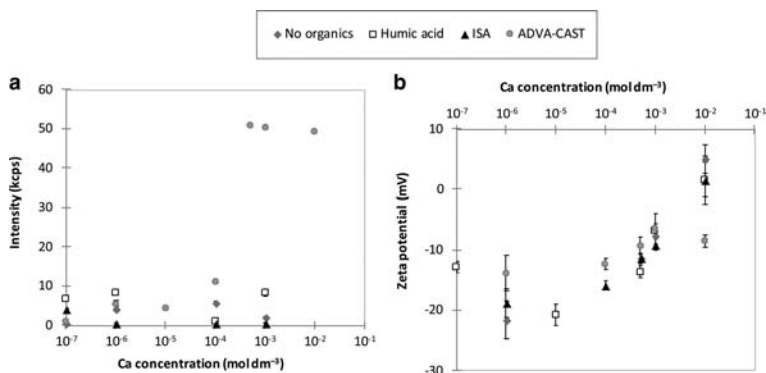


FIG. 4. Stability of Fe<sub>2</sub>O<sub>3</sub> colloids as a function of the concentrations of Ca (as Ca(NO<sub>3</sub>)<sub>2</sub>) (a) light scattering and (b) Zeta potential.

added to silica and Fe<sub>2</sub>O<sub>3</sub> in 0.05 NaOH + 0.05 KOH mol dm<sup>-3</sup> suspensions, mimicking the composition and pH of a fresh cement pore water. In the case of silica, the presence of Ca caused no further precipitation of the colloids and the Zeta potential remained almost constant around -10 mV, and no differences were observed in the presence of organics. However, in the case of Fe<sub>2</sub>O<sub>3</sub> (Fig. 4a), whilst at pH 13 all colloids had precipitated, the presence of ADVA<sup>®</sup> Cast 550 caused the re-stabilization of Fe<sub>2</sub>O<sub>3</sub> at concentrations of Ca higher than 10<sup>-3</sup> mol dm<sup>-3</sup>. At pH 13, the addition of Ca caused a steady increase of the Zeta potential of Fe<sub>2</sub>O<sub>3</sub> (Fig. 4b) going from -25 mV to positive values around +5 mV, with the only exception of the experiments in the presence of ADVA<sup>®</sup> Cast 550 where the Zeta potential remained negative between -15 and -10 mV in the whole range of added Ca<sup>2+</sup>. This behaviour in the absence of an organic compound was also observed by Gardiner *et al.* (1992) who reported an increase in the Zeta potential value of hematite colloids in 10<sup>-3</sup> mol dm<sup>-3</sup> NaOH as a result of the addition of cement leachates and specific sorption of Ca<sup>2+</sup>. In the present work, it would seem that ADVA<sup>®</sup> Cast 550 may be preventing the sorption of Ca<sup>2+</sup> to the surface of the Fe<sub>2</sub>O<sub>3</sub> colloids either by sorbing itself to the surface of the colloids or by complexation with Ca<sup>2+</sup> and hence, limiting the amount of Ca<sup>2+</sup> free to sorb to the colloids. It has been reported that in natural systems, the stability of iron oxides is controlled by humic substances (Tipping and Ohnstad, 1984). Tiller and O'Melia (1993) reported the increase in the stability of Fe<sub>2</sub>O<sub>3</sub> colloids in the presence of two linear polyelectrolytes (poly (aspartic) and poly (acrylic) acid), used as models of natural organic matter (NOM) due to sorption to

the particles under acid conditions and alteration of the net surface charge, stabilizing particles by electrostatic repulsion between negatively charged surfaces. However, the authors observed that even in the presence of NOM, Ca<sup>2+</sup> caused destabilization of Fe<sub>2</sub>O<sub>3</sub> by complexation with the anionic groups of the organic compounds and reducing the electrostatic repulsion that kept the colloids in solution (Mylon *et al.*, 2004). In the present work, such stabilizing effects by humic acid could not be observed at pH 13, since at this pH the net charge on the surface is negative as can be inferred from the Zeta potential data in Fig. 3b and d, limiting the sorption of NOM to the colloids.

Gardiner *et al.* (1992) investigated the stability of model Fe<sub>2</sub>O<sub>3</sub> colloids in Volvic water in the presence of 100 ppm humic acid or the alkaline degradation leachate from wood with an equivalent organic content of 100 ppm as total organic carbon (TOC), observing in both cases a noticeable increase in the stability of the colloids. Unfortunately, the authors did not provide data on the pH or the composition of the solutions; therefore it is difficult to compare these observations with the present work. However, it must be noted that the concentrations of humic acid and wood degradation products were higher than the ones used here (5 ppm HA and 10<sup>-3</sup> mol dm<sup>-3</sup> ISA, equivalent to 72 ppm TOC). Moreover, Gardiner *et al.* (1992) attributed the stabilizing effect of the organic compounds to steric repulsion between sorbed organic layers on the surface of the hematite, while in the present work the Zeta potential data in Fig. 3b and d suggested that there was little (in the case of ISA) or no sorption of the organic compounds to the colloids, as the Zeta potential remained very close to the one in the absence of organic matter.

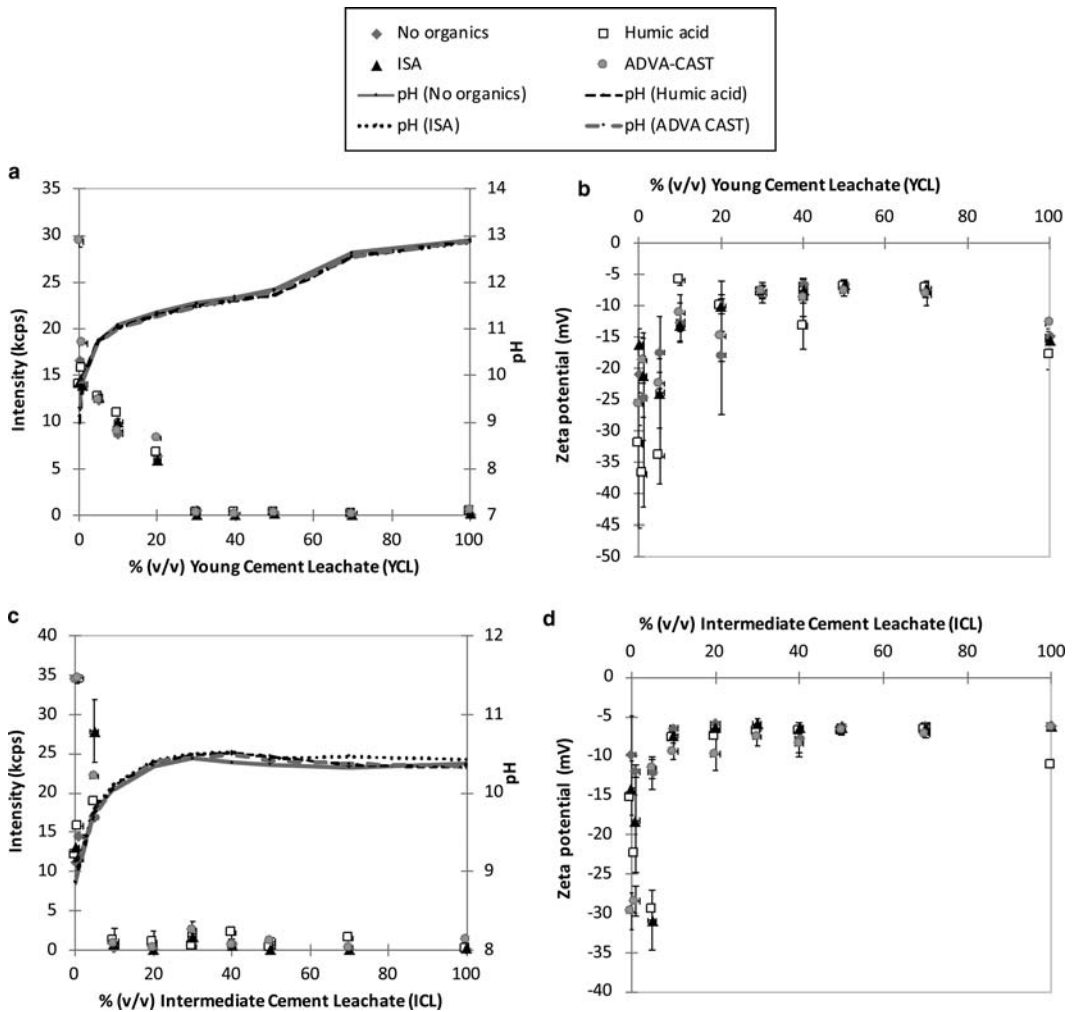


FIG. 5. Light scattering intensity and Zeta potential as a function of the percentage of cement leachate for silica colloids in the presence of YCL (a) light scattering and (b) Zeta potential and in the presence of ICL (c) light scattering and (d) Zeta potential.

#### Addition of cement leachates

In order to mimic a situation in which an intrusion of cement leachates reaches the colloids present in the host rock in the proximity of a cementitious repository, increasing proportions of either YCL or ICL were added to the silica and  $\text{Fe}_2\text{O}_3$  in  $0.01 \text{ mol dm}^{-3} \text{ NaClO}_4$ . Figure 5 shows that the addition of YCL to the silica colloids caused a steady precipitation of the particles, which flocculate completely at percentages of YCL higher than 30% v/v, and the effect of ICL is even more acute, with 10% v/v ICL causing complete precipitation of the colloids. The trends observed with the light

scattering (Fig. 5a and c) were mirrored by the Zeta potential data (Fig. 5b and d), where the addition of the leachate modified the charge on the surface of the colloids from a Zeta potential around  $-30 \text{ mV}$  to values between  $-10$  and  $-5 \text{ mV}$ , and the ICL, which has a higher concentration of  $\text{Ca}^{2+}$ , caused a faster change in the surface charge. This behaviour could be explained due to the sorption of  $\text{Ca}^{2+}$  to the silica. There were no differences observed in the behaviour of the silica colloids in the presence and absence of organic compounds, which may suggest the lack of affinity of the silica colloids for this type of organic compounds. The  $\text{Fe}_2\text{O}_3$  particles

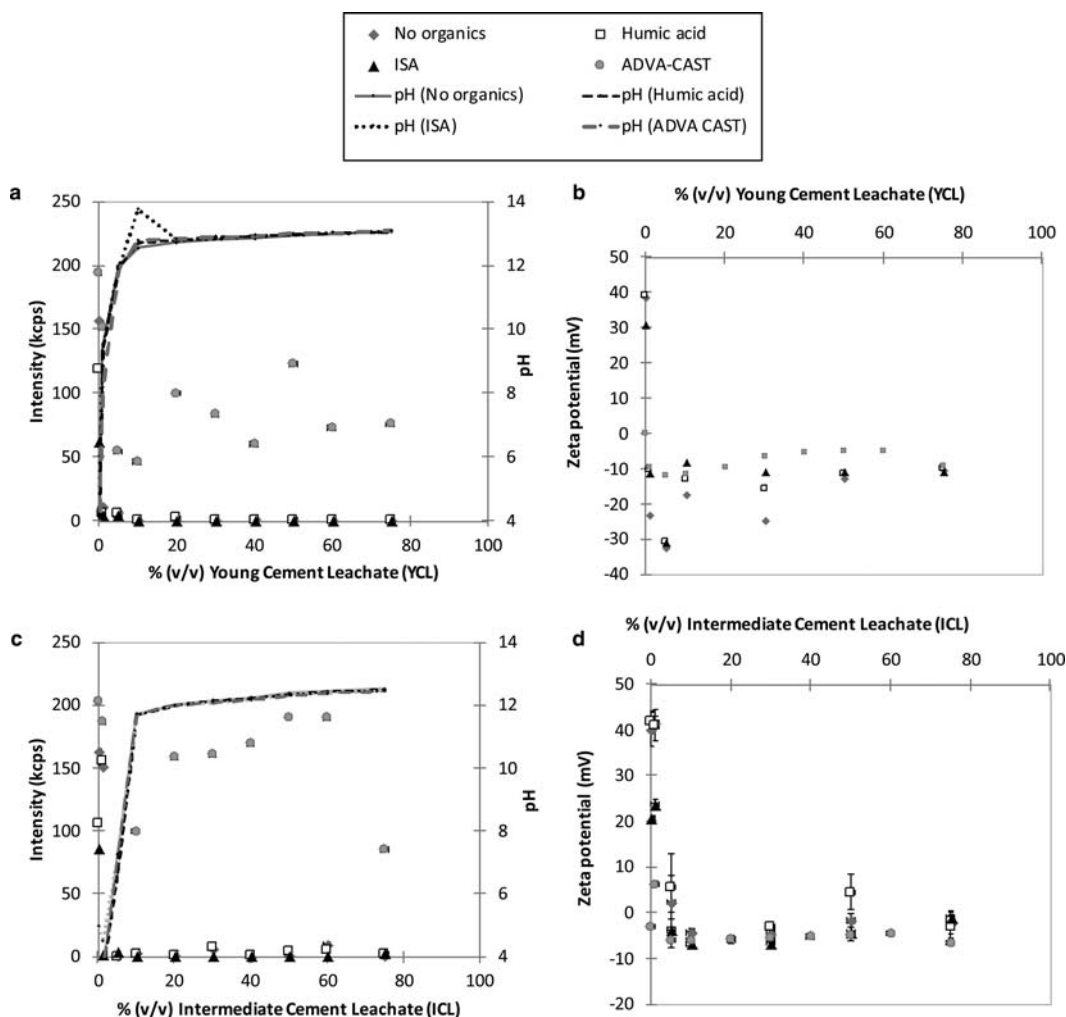


FIG. 6. Light scattering intensity and Zeta potential as a function of the percentage of cement leachate for  $\text{Fe}_2\text{O}_3$  colloids in the presence of YCL (a) light scattering and (b) Zeta potential and in the presence of ICL (c) light scattering and (d) Zeta potential.

were more sensitive to the presence of YCL and ICL, and 1% v/v of any of the leaches was enough to cause complete precipitation of the colloids (Fig. 6). As in previous experiments ADVA<sup>®</sup> Cast 550 increased the stability of  $\text{Fe}_2\text{O}_3$  in the presence of the cement leachates. Comparing Fig. 6a and c, it can be observed that the extent of the ADVA<sup>®</sup> cast 550 stabilization effect was greater in the case of ICL than YCL, which may be related to the concentration of  $\text{Ca}^{2+}$  as suggested by the results in Fig. 4. ADVA<sup>®</sup> Cast 550 managed to maintain the Zeta potential of the  $\text{Fe}_2\text{O}_3$  particles almost constant

in the whole range of added YCL and ICL (Fig. 6b and d), while in the other experiments the addition of the leachate very quickly changed the Zeta potential from a positive value between +20 and +40 mV to neutral or slightly negative potentials.

## Conclusions

This work on the stability of model colloids, silica and  $\text{Fe}_2\text{O}_3$ , showed that under the conditions of the ADZ, these colloids were very unstable and tended

to precipitate. This behaviour, seen under batch conditions, fitted with the observed lack of colloids generated from the treatment of sandstone cores with cement leachates under flow conditions. The stability of silica seemed to be more affected by the nature and concentration of the counter ions in solution, while the main factor governing  $\text{Fe}_2\text{O}_3$  seemed to be the pH. The presence of humic acid and ISA at the levels tested here did not affect the stability of the colloids under ADZ conditions; however the presence of the cement additive ADVA<sup>®</sup> Cast 550 increased notably the stability of the colloids against the increase of pH and Ca concentration.

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