

Retention of Cr in Metakaolin-based Geopolymeric Materials under Oxidation and Carbonation – 17453

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ABSTRACT

Alkali activated alumino-silicates, often referred to as geopolymers, are considered promising immobilization matrices for contaminants due to their high sorption capacity, durability and low leachability. For some contaminants they may prove superior to cement pastes that are conventional immobilization materials in waste management applications.

However, estimating the retention capacity of some contaminants under environmental conditions that include oxidation and carbonation and may induce a valance change, is complicated. These contaminants tend to be soluble under oxidizing condition and form precipitates under reducing conditions. Thus, contaminant retention is highly dependent on the initial oxidation state at which the metal was introduced, as well as the matrix sorption ability, ability to resist oxidation and carbonation, and the contaminant leachability. Moreover, carbonation in considered one of the most important degradation mechanisms in cementitious material, causing porosity reduction and significant changes in contaminant leachability, however, geopolymers have considerably lower Ca content relative to cements, or none, and the effect of carbonation on these pastes is less clear. Thus, contaminant release mechanisms and rates must be estimated based upon exposure to various atmospheres appropriate to waste management applications.

In this study we aim to estimate the sorption capacity, and leachability of Cr from a metakaolin based geopolymer, doped with Cr, as a function of its oxidation state and carbonation. Cr has a high valance range from +6 to 0 similar to Tc, and is used as its simulant in the current study. Sodium dichromate was used as an oxidized source metal material. To induce reducing conditions, ascorbic acid was added except for experimental control cases. The samples were aged under N₂, 98% N₂ + 2% CO₂, CO₂ deficient air and air environments under constant relative humidity. Following aging, samples were subject to equilibrium leaching as a function of pH (EPA Method 1313) and monolith mass transport rate testing (EPA Method 1315).

Mass balance calculations, based on the results of a pH dependent leaching test, have shown that oxidized Cr samples lost 85-95% of their Cr content, whereas, the reduced Cr samples lost only 20% of their Cr content. On the other hand, the leachability of Si and Al is much higher in the reduced-Cr samples then in the samples with oxidized Cr, and their natural pH is up to 2.5 pH units lower than that of the oxidizing cases. Thus, we conclude that the combination of the reducing agent and the spike chemistry influence the matrix formation. Sample aging have not resulted in any significant

change in the Cr-leaching behavior of the oxidizing matrices in the pH dependent leaching test, although a significant decrease in the natural pH, of 1.5 pH unit, was observed upon exposure to elevated CO₂ levels (2%), probably due to the formation of Na-carbonate species. The pH and leaching behavior of the reduced Cr samples under the various aging conditions have not yielded significant variation either in their natural pH or in their leaching behavior.

INTRODUCTION

Geopolymeric matrices are considered as alternative retentive wasteforms for radioactive waste contaminants, traditionally sequestered in cementitious materials [1, 2]. Geopolymers are alkali activated matrices that consist mainly of silica and alumina. They can be produced from Si-Al rich source materials that dissolve in an alkali solution such as clay or fly ash. Geopolymers consist of a polymeric silicon-oxygen-aluminum framework, not unlike that found in zeolites, with alternating silicon and aluminum tetrahedra joined together in three directions by sharing all the oxygen atoms [1]. Additionally, the fact that the Al (+3) valance is lower than that of the Si (+4), an extra stabilizing alkali element (Na or K) is needed for the geopolymer structure. Unlike zeolite synthesis, geopolymerization is conducted in highly alkaline solutions and at a relatively low solution-to-solid ratio (low water content) which result in rapid polymerization without sufficient time to form an organized crystal structure. This results in a microcrystalline to amorphous structure [1]. Moreover the Si/Al ratio of the material effects its polymerization where high Si/Al ratios tend to yield more amorphous material.

The characteristics of the geopolymers are related to their source material, to the alkalinity and pH of their activation agent and the specific Si/Al ratio in the cast. Geopolymers were studied for the disposal of radioactive waste in Europe in the late 1990's [2]. Geopolymers, with a Si:Al ratio between 1:1 and 2:1, were considered as treatment options for high valance metals such as Ni, Se, Ba, Cd and Cr under RCRA treatability testing with leaching test results meeting TCLP toxicity characteristic requirements although the binding mechanism was not clear [2].

Metakaolin based geopolymers were studied for their encapsulation capacity for Cs-137 and Sr-90 [3]. They showed that the Cs was incorporated in the amorphous phase, whereas Sr was partially crystalline as a carbonate. Thus, different elements may be attached to the geopolymer via various binding mechanisms. Geopolymer formulations were also studied for the retention of Tc, with Re used as a surrogate [4], but gave unclear results with respect to these elements.

Redox sensitive radionuclides are extremely complicated to retain. Runde [5] have shown that most actinides are relatively insoluble when reduced but highly mobile in solution when oxidized. This effect is enhanced in the presence of carbonate species in solution which creates highly soluble carbonate complexes with high valance actinides (e.g. U). As an example, Zavarin et al., [6] have studied the implication of oxidation state on colloid formation and mobility through a dolo-stone fractured rock core. They have shown that actinides at different oxidation states show significantly different precipitation and mobility behaviors as colloids in the presence of carbonate species. Tc is highly mobile when oxidized but relatively well retained when reduced [7]. Technetium may exist at eight oxidation states with the most common ones being (IV), (V) and (VII). The main concern about Tc is the long lived Tc-99 isotope

($t_{1/2}=211$ ka). Cr is a redox active transition metal with similar chemical characteristics as Tc, and thus can be indicator surrogates to this highly radioactive element in experiments. It has a wide range of oxidation states, from zero in their metal form to +6 in its most oxidized condition.

In this research we aim to study the retention capacity of metakaolin based geopolymer for Cr as a simulant for Tc. Cr was introduced both in its oxidized (C(VI)) and reduced (Cr(III)) state, in order to estimate the impact of oxidation. We studied retention ability of the material after curing and aging under different environments, resulting in carbonation and oxidation of the matrix, which may occur during various disposal scenarios.

METHODS

Experimental methods

The main Si-Al source of the geopolymer used was metakaolin (MK) calcined from purified kaolin clay, which was supplied by Advanced Cement Technologies (PowerPozz™). The chemical composition and physical properties of the metakaolin are presented in Table I and Table II, respectively.

Table I: Chemical composition of raw metakaolin given in wt% of oxides (manufacturer data)

SiO₂	Al₂O₃	Fe₂O₃	CaO	TiO₂	MgO	Na₂O	K₂O	P₂O₅	SO₃	LOI^a
51-53	42-44	< 2.20	< 0.20	<3.00	<0.10	<0.05	<0.40	<0.20	<0.50	<0.50

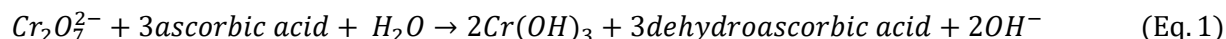
^a LOI: loss on ignition, 950 °C

TABLE II: physical characterization of raw metakaolin

BET [m²/g]	Density [g/cm³]	Particle diameter < 45 [μm]	Particle diameter > 45 [μm]	Mean particle diameter [μm]
23.5	2.6	28.37 wt. %	71.63 wt. %	11.535

The alkali activator is composed of sodium silicate solution and NaOH. The Si/Al ratio of the cast and the Si/Na ratio are given in Table III.

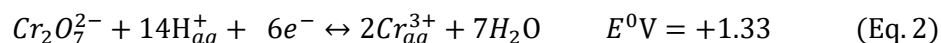
The casts were spiked with Cr. Na-dichromate was used as source material for Cr. The samples were doped to a level of 0.5 and 1 wt. % for reduced and oxidizing samples respectively (Table III). Ascorbic acid was added to the cast as a reduction agent for Cr. Under alkaline condition the reduction mechanism for Cr(VI) is [8]^{1, 2}:



Where

1 dehydroascorbic acid -C₆H₆O₆

2 ascorbic acid - C₆H₈O₆



The molar ratio between Cr and ascorbic acid is 2/3. The amount of ascorbic acid in this experiment was calculated to exceed this value to ensure full reduction where the ascorbic acid was not a limiting factor. Moreover, Xu et al., [8] have shown decreased reduction capacity of the Cr (VI) at highly alkaline conditions expected in this system, thus, excess ascorbic acid was necessary. However, the excess acid and the dehydroascorbic acid resulting from reaction are expected to lower the overall pH of the system.

Table III: Compositions of cast materials used in this study.

Cast	Un-spiked	1	2	3	4
Spike conditioning		oxidized	oxidized	reduced	reduced
Cast date (year 2016)	March 2 nd	March 30 th	March 30 th	April 13 th	April 13 th
Sodium silicate (g)	608	413	413	413	413
NaOH (g)	100	52	52	52	52
Metakaoline (g)	499	344	344	344	344
Na ₂ Cr ₂ O ₇ ·2H ₂ O (g)		26	26	13	13
H ₂ O (g)		34	34	21	21
C ₆ H ₈ O ₆ ascorbic acid				45	45
Total mass (g)		868	868	886	886
Si/Na (mol ratio)	1.53	1.67	1.67	1.72	1.72
Si/Al (mol ratio)	1.66	1.66	1.66	1.66	1.66
Cr/ascorbic acid (mol ratio)				0.33	0.33
Cr wt%		1	1	0.5	0.5
Na mol/Kg	3.79	3.31	3.31	3.14	3.14
Cr mol/Kg		0.2	0.2	0.09	0.1

Casting procedure: All casting and curing procedures were carried out at the Ben Gurion University, Israel. NaOH was dissolved in sodium silicate solution and left to cool for an hour. Metakaolin powder was manually mixed with the alkali solution in a fume hood. The metal salt was dissolved in MQ water and the resulting solution was added to the metakaolin-sodium silicate mixture. For the reduced casts, ascorbic acid was added, and the casts were mixed to homogenize. Each of the Cr bearing geopolymer compositions was cast in two batches (Table III). The paste was poured into the tubes and extracted after 7 days. After extraction from the tubes the samples were left to cure under N₂ atmosphere at 100% humidity for 90 days. 450 g of each

composition was crushed in order to perform the 1313 EPA test. From the remaining tubes, the top 5 mm were dry-cut off to create a pristine surface for leaching under the 1315 EPA test.

Porosity and relative humidity (RH) measurements: Porosity and open porosity at a specific relative humidity were measured based on the methods described in [9]. One tube of each composition was cut perpendicular to its long axis, creating circular disks. The geometric dimensions of the sample were measured (diameter was fixed by the tube shape and height was measured using a micrometer). Each disk was weighed and then dried under vacuum until no further weight change was registered. Then the sample was put in a sealed vessel with MQ water at the bottom to achieve 100% RH at room temperature; the samples then were maintained under these conditions until no further weight change was registered. The porosity of the sample was calculated as follows:

$$\text{porosity [\%]} = 100 \times \frac{\frac{\text{Wet weight [g]}}{\text{volume [ml]}} - \frac{\text{Dry weight [g]}}{\text{volume [ml]}}}{\frac{\text{Wet weight [g]}}{\text{volume [ml]}}} \quad (\text{Eq. 3})$$

The relative saturation under 33% and 68% RH was measured using a similar process, where the samples were equilibrated within a sealed vessel at 100% RH, and then transferred into sealed vessels over saturated solutions of MgCl (33% RH) and NaNO₂ (68% RH), and the weight change between the two conditions was registered and relative saturation calculated.

Aging procedure: Both cut monolith and crushed samples were aged for 60 days at four different aging atmospheres: air; CO₂-free air; 2 vol % CO₂ in N₂, and N₂. A humidity of 68% was maintained in all the aging chambers. Air and CO₂-free air conditions were maintained inside Fisher Scientific Isotemp Model FFTG500RTABC incubators with beakers of supersaturated NaNO₂ solution at the bottom of the incubator to maintain 68% RH. The 2% CO₂ and N₂ conditions were maintained in pressure vessels (Central Pneumatic 2.5 gallon Air Pressure Paint Tank) fitted with an inlet and outlet. The gas was bubbled through MQ water to yield 100% RH gas phase, then the humid gas was mixed with dry gas to create a 68% RH environments. The gas continuously flowed through the chambers at a rate on 40 cc/min enabling four volume changes per day. The humidity was monitored weekly. In order to maintain "as is" conditions at the end of 60 days of aging, the samples were kept in similar chambers under N₂ at 68% RH, to prevent reaction until further analyses were conducted. In addition two ground samples were kept under 100% RH in N₂ for a short period and then tested using the EPA 1313 leaching procedure in order to observe the un-aged behavior of the samples.

EPA 1313 leaching procedure: Crushed samples (85wt% < 2 mm) were leached according to the EPA 1313 leaching procedure. The aim of this test is to create a wide range of pH dependent leaching conditions, between pH 2 and 13, to determine

liquid-solid partitioning as a function of end-point pH. Crushed material was weighed into 50 ml tubes. Nitrogen bubbled MQ, acid (2 N HNO₃) and base (1 N KOH) solutions were added to the weighed samples, to create an overall 1:10 ratio of solid to liquid. The samples were rotated in an end-over-end tumbler for 48 hours at room temperature. The pH and EC of the samples were measured using a Thermo Fisher Scientific, Accumet XL20 device. The samples were centrifuged (4000 rpm, 15 min), and decanted. The decanted solution was filtered through Environmental Express Flipmate Filtration Assembly; 0.45 µm; PES filter and analyzed for major elements using ICP-OES.

EPA 1315 leaching procedure: cut samples, with one surface exposed were leached using a 1-D configuration of the EPA 1315 leaching method. A plastic tube was attached to the exposed surface of the samples making an interaction vessel. 45 ml of bubbled MQ was poured into the interaction vessel, leaving a minimal amount of head space. The solutions were exchanged after 2 hours, 1, 2, 7, 14 (28, 42, 49, and 63) days. The pH, EC and ORP of the samples were measured. The samples were centrifuged and analyzed using ICP-OES for major elements.

Analytical methods

ICP-OES: elemental concentrations were measured using a couple plasma-optical emission spectrometry (ICP-OES) using a Varian ICP Model 720-ES. Five-point standard curves were used. Analytical blanks and analytical check standards at approximately 0.5 mg/L were run every 20 samples and required to be within 15% of the specified value. 10 mg/L Yttrium was used as the internal standard. One analytical matrix spike was checked for each replicate set of analytical samples of a leaching test (i.e., approximately one spike for every ten analytical samples). The estimated error for major elements is 10% and for trace elements is 15%.

RESULTS

Porosity and relative saturation

The porosity and the relative saturation of the different materials were calculated. The total porosity estimated for the three materials is identical within error; the relative saturation at different relative humidities is lower for the spiked material with respect to the un-spiked probably due to spike leaching and dissolution.

Un-spiked geopolymer material

A smooth pH curve is observed for this material, the natural pH of the geopolymer is 12.4. As the pH lowers, silica gel starts to form, where at pH of 2.5 all the material becomes gel, with only a very small amount of liquid left (Fig 1). The concentrations of the major ions are given in Figure 3. The concentration of both Al and Cr increase steeply at pH 3, and the Si concentration drops, due to Si fractionation into the gel

TABLE IV: the porosity and the relative saturation of the materials at different relative humidity

Material	Porosity [%] ($\pm 5\%$)	Relative saturation [%] at 33% RH ($\pm 5\%$)	Relative saturation [%] at 68% RH ($\pm 5\%$)
Non spiked geopolymer	22	86	90
Oxidized Cr	21	82	87
Reduced Cr	22	80	84

phase. At higher pH values Si and Al show a similar trend where concentrations are higher at the low and high pH ends of the range and relatively low at the middle of the pH range. Cr closely mimics the Al trend, however, its concentration begins to rise at pH 7.8 and the Al concentration remains low up to pH values higher than 10. Na maintains a high concentration throughout the leaching test. The lowest concentration is measured at the natural pH and the highest one is measured at pH 5.5 where the concentrations of the other major elements are minimal.

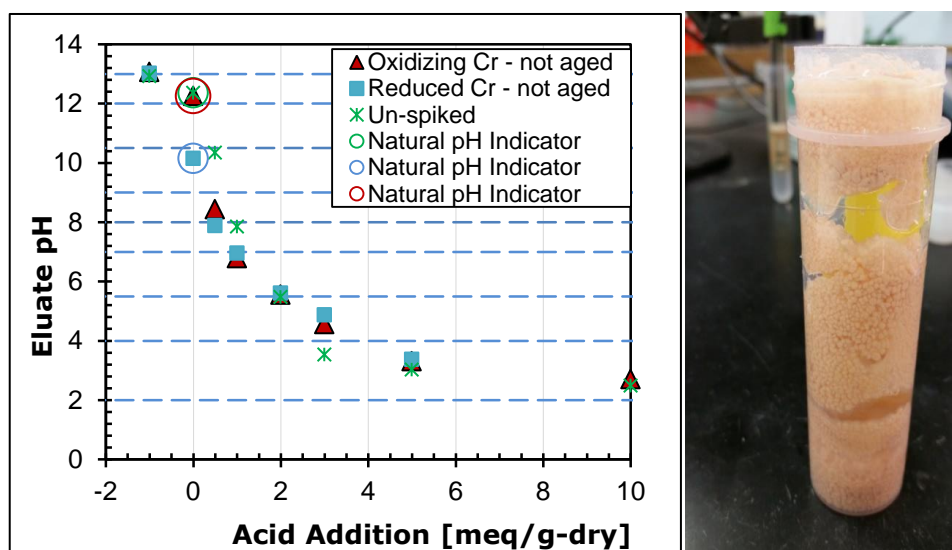


Fig 1. Right: Titration curve for un-spiked, oxidized-Cr and reduced-Cr samples from Method 1313 results (no aging). Left: silica gel formation at pH 2.5.

Oxidized-Cr and reduced-Cr samples (no aging)

A 1313 leaching test was performed for the crushed Cr sample without aging. Figure 1 shows the pH titration curve obtained for both tests. The two pH titration curves are almost identical, however a large deviation between the two curves is observed at the natural pH level, where for the oxidized Cr sample the natural pH is at 12.3, similar to the pH obtained for the non-spiked material, however for the reduced Cr sample the natural pH is significantly lower, at 10.2, due to the addition of the ascorbic acid as a

reducing agent. However, at low acid addition during the Method 1313 test (0.5-1 meq/g) the endpoint pH of the un-spiked material is significantly higher than both Cr-spiked materials, which may result from the Cr addition itself or the different curing conditions (under atmospheric and inert conditions). An additional difference between the two sets was in the low pH range where a thick gel developed at high acid addition in the reduced Cr sample, whereas a fine gel form, that looked like a suspension evolved for the oxidized samples.

Figure 2 shows the solutions acquired from the 8 test positions for the oxidized Cr samples. A clear color change can be seen along this range. This change is probably due to change in the Cr^{+6} speciation where at high pH CrO_4^{2-} is the dominant species (yellow) and at low pH HCrO_4^- is dominant (orange) [quantification in-progress].

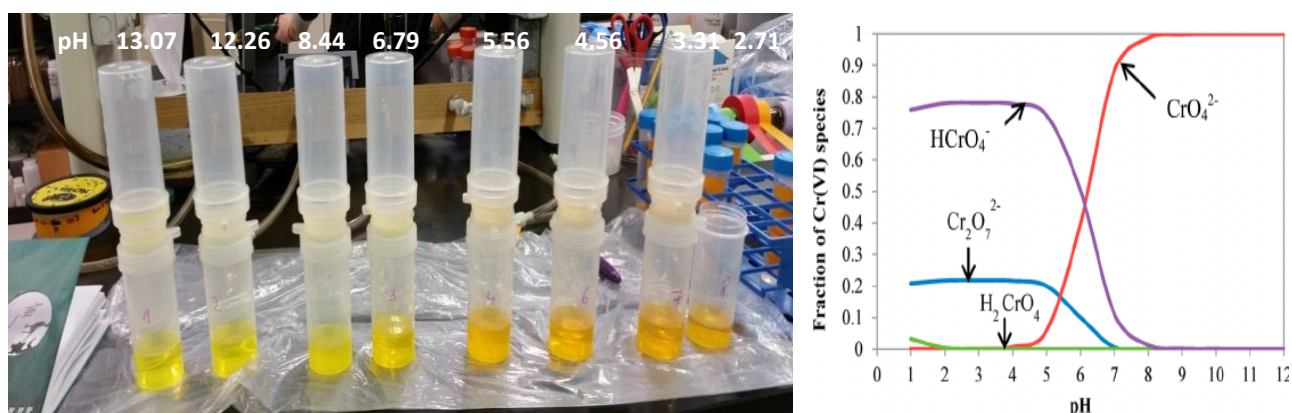


Fig 2: (Left) 1313 EPA method leachate solution color change, for a set of oxidized Cr spiked, un-aged samples. The samples pH is indicated on the figure. (Right) theoretical speciation variation of Cr in aqueous solution across the pH range [10].

Figure 3 shows the major elements concentration variation for the two experimental sets. When observing the two major constituents of the matrix, Si and Al, a significant difference between the reduced and oxidized casts arises. For both elements the minimal concentration is measured at the natural pH where the sample is the most stable. For the reduced sample the concentration of both elements rises by 1-2 orders of magnitude at low pH. However, for the oxidized sample the concentration of both Si and Al is low throughout the pH range, with an Al increase at the most acidic conditions probably due to Si removal from the solution and solution consumption for gel formation. This behavior is identical to the one observed for the un-spiked sample. The Na concentration in the two sets of spiked samples is identical at $\text{pH} \geq 4.9$ while the Na concentration in the reduced sample increases at $\text{pH} < 4.9$, whereas the Na concentration in the oxidized sample decreases slightly. For both samples, these values are significantly higher than the value measured for the un-spiked sample. This phenomenon is interesting as the Si/Na ratio of this cast is actually slightly lower, this

may hint some structural changes in the sample that make Na more available in the later cases. However, the shape of the curve – e.g. concentration decrease at low pH is similar for both oxidized Cr cast and the un-spiked cast.

The Cr concentration in the leached solution from the oxidized sample is an order of magnitude higher than that of the reduced sample across the pH range of the Method 1313 test. A slight change in concentration is observed at the lower most pH, however, overall no pH dependent fractionations are observed. Regarding the different doping level of the two samples (i.e. 0.5wt% and 1wt% for the reduced and oxidized respectively) 5 times more Cr is leached from the oxidized material.

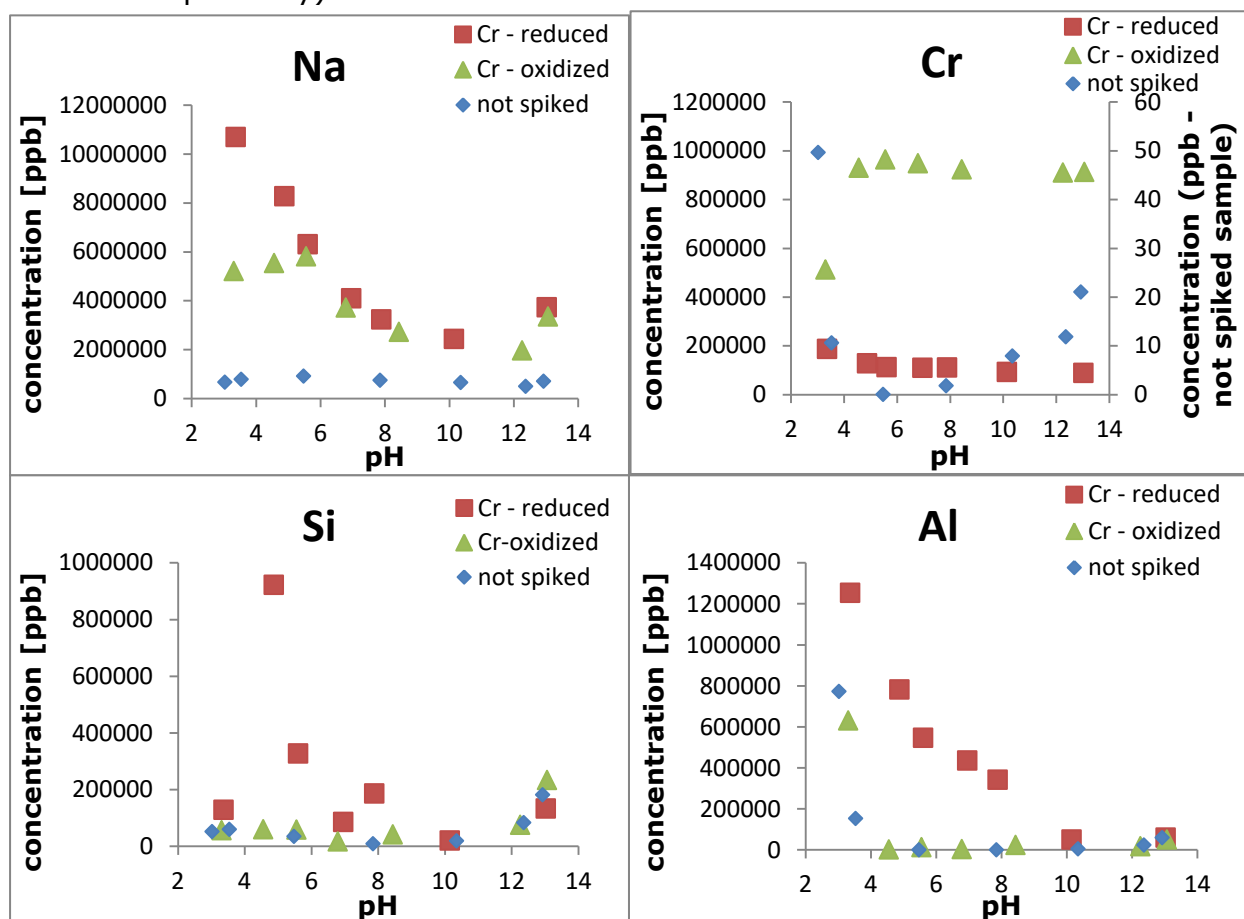


Fig 3. Element leaching as a function of pH for major matrix constituents (e.g. Al, Si, Na and Cr) based on Method 1313 results for the un-spiked, oxidized Cr and reduced Cr samples.

Sample Aging

After aging under the different environments, one monolith sample of each composition and aging condition, was cut parallel to its long axis and was photographed using a binocular microscope (Fig 4). The sample spiked with oxidized Cr showed no front evolution in the material under the different pH conditions. However

the reduced Cr samples showed the development of an ingress front under both air and CO₂-free air conditions. Figure 4 shows the developed fronts for each aging condition. The front for the samples aged under the CO₂-free air condition looks spotty, where dark spots penetrating the sample to a depth of 0.5-1.5 mm. For the sample aged under air, the front is more continuous and loses the spotty texture. The sample is darker in the front area and comes back to its bulk color ~1 mm from the edge. The samples aged under CO₂ were not yet processed at the time of preparation of this paper.

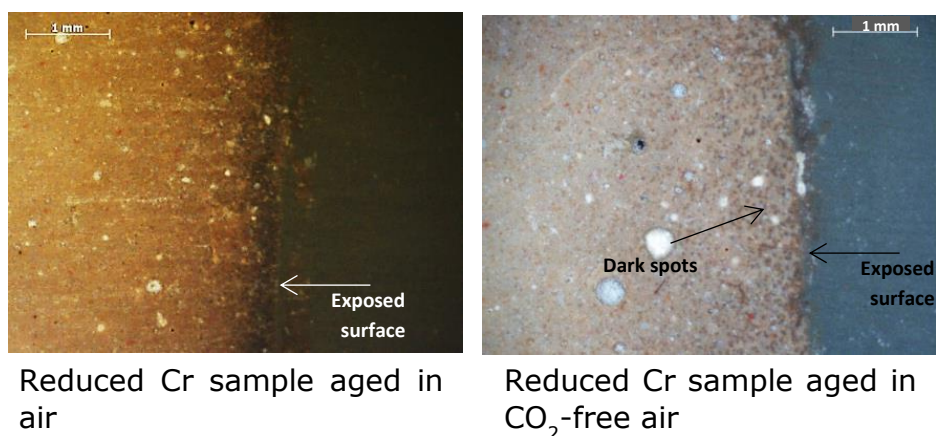


Fig 4. Optical images of the reacted front ingress for reduced Cr bearing samples under air and CO₂ free air conditions.

Oxidized-Cr and reduced-Cr 1313 leaching test after aging

A 1313 leaching test was performed for the crushed samples after 60 days of aging under various conditions. In spite of the observed oxidation front in the reduced-Cr samples exposed to oxygen (i.e. air and CO₂ free air conditions), no significant variation in the leaching behavior was observed for the different elements under the various aging condition. Figure 5a shows the titration curve of reduced and oxidized Cr samples aged under different condition, as well as the un-aged samples. The curves are essentially identical, except for a variation at the natural pH (Fig 5b). This variation is similar to the one seen for the un-aged material. All the reduced-Cr samples have similar natural pH of $\sim 9.9 \pm 0.1$. For the oxidized Cr samples, there is a gradual decrease in the natural pH, where the highest pH is measured for the sample aged under N₂, with lower pH for the samples aged under O₂ and the lowest pH for the carbonated sample. As was mentioned before, the strong decrease in natural pH between the oxidized and reduced samples results from access ascorbic acid addition in the casting procedure.

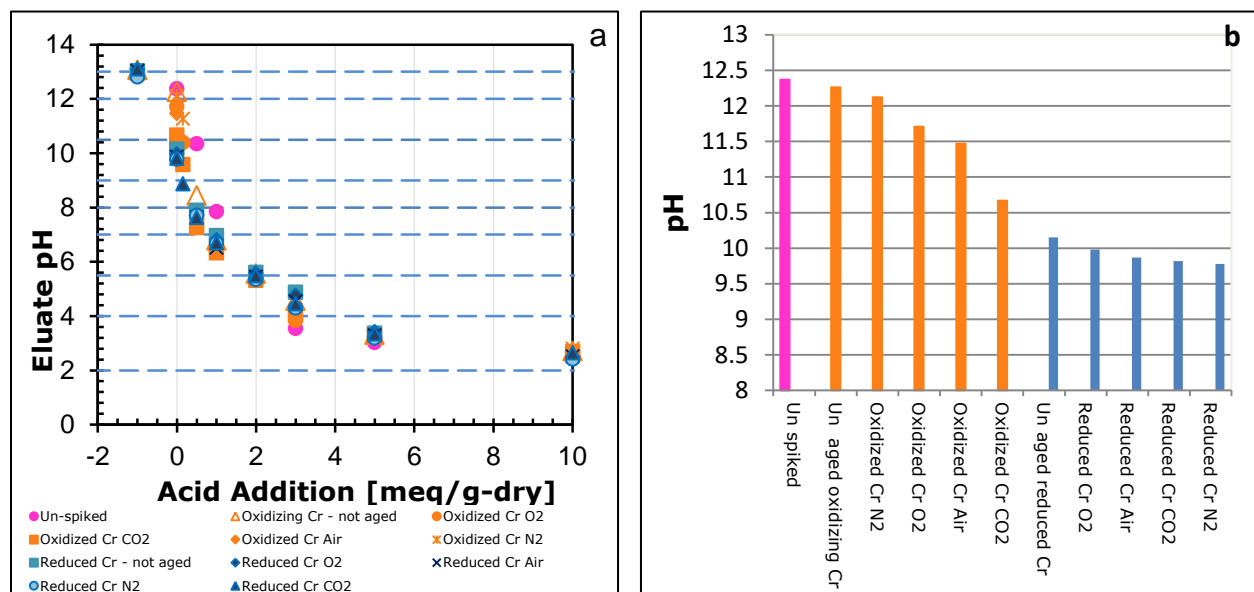


Fig 5. a) Effects of aging on the pH titration curve for various samples. b) Natural pH of the different samples

All of the reduced-Cr samples have a similar major element leaching behavior across the pH range with no clear effect of the ageing conditions (Fig 6). The oxidized Cr samples behave the same. However, a significant difference in the leaching behavior of the different elements is observed between the two matrices. The oxidized samples show lower leachability of Al and Si at the intermediate pH range (4-8) with respect to the reduced samples. The un-spiked material behaves similar to the oxidized-Cr spiked matrix. The Na leaching for both Cr-spiked materials is similar, whereas the Na leaching from the oxidized un-spiked sample is significantly lower. The Cr leachability is an order of magnitude higher for the oxidizing samples with respect to the reduced Cr ones.

Oxidized-Cr and reduced-Cr 1315 leaching test after aging

Sixteen monolith samples were exposed to a 1D leaching test. The samples represent duplicates of the four atmospheric aging conditions and two types of matrices, e.g. reduced Cr and oxidized O₂ Cr. Figure 7 presents the percent of the initial Cr content leached from the samples. It can be seen that all the oxidized Cr samples have leached significantly more Cr with respect to the reduced ones. After 14 days, samples that were not exposed to oxygen (i.e. CO₂ and N₂ environments) have leached more than samples that were exposed to oxygen. The former have leached 11-14% of their initial Cr content, whereas the latter have leached only 5.5-8.5%. The reduced Cr samples have leached significantly smaller amounts (1 -3%) with no clear variation between the different aging conditions. This is true in spite of the reaction front observed visually.

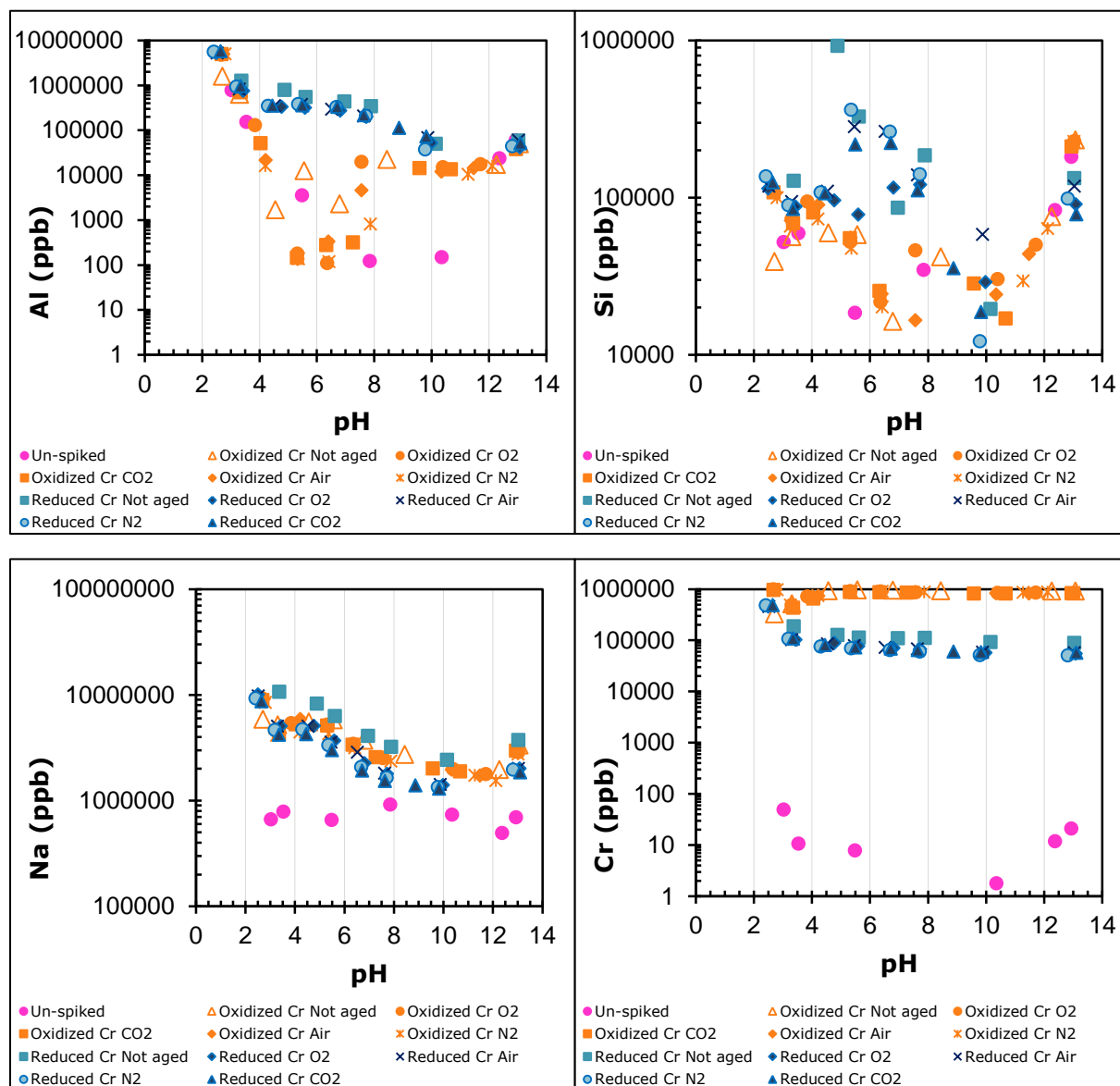


Fig 6. Element leaching as a function of pH for major matrix constituents (e.g. Al, Si, Na and Cr) based on Method 1313 results for aged Cr bearing matrices.

DISCUSSION

Cr mass balance

Mass balance calculations were conducted based on the initial concentration Cr in the samples. Based on the pH dependent leaching test (EPA 1313), the unaged oxidized Cr samples lost 95% of their Cr content, whereas, the reduced Cr samples lost only 20% of their Cr content. For the aged samples, the values are 85% for the oxidized samples and 20% for the reduced ones. The difference between the aged and unaged

material for samples cast with the same formulation and aged under N₂, a non-reactive environment, can be related to the matrix changes due to longer time from casting.

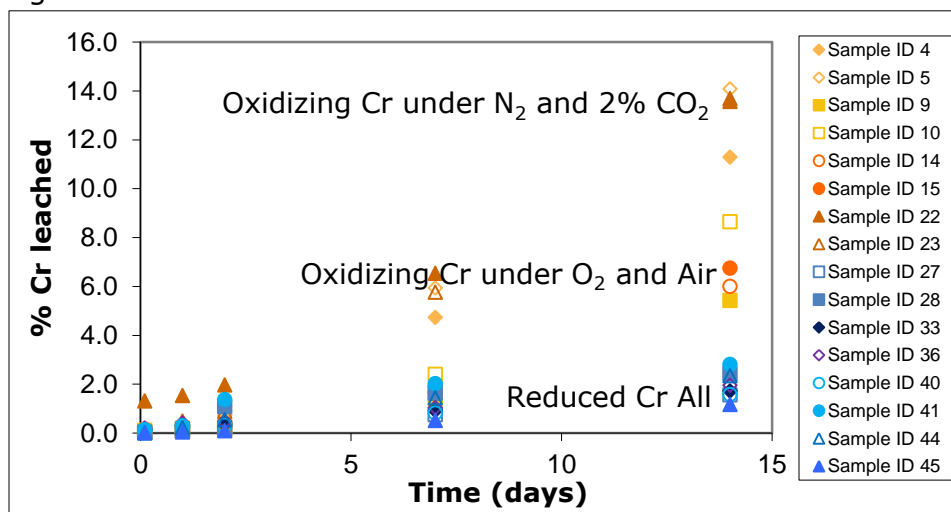


Fig 7. Cr leaching during the first 14 days of the leaching experiment. Duplicate samples have the same symbol and color with filled and empty symbols. All reduced Cr samples are in shades of blue and oxidized Cr samples are in shades of orange.

This result is not surprising as the solubility of oxidized Cr (73 g/100 mL at 25 °C) is higher than that of the reduced species Cr(OH)₃ which is relatively insoluble in water. The monolith leaching, time dependent experiment (EPA 1315), enhances this conclusion, where only up to 3 wt% for the Cr was leached from the reduced material while up to 14 wt% was leached from the oxidized material, during the initial two week of testing.

Matrix effect

The leachability of Si and Al is higher in the reduced-Cr sample than in both the un-spiked sample and the sample with oxidized Cr. Additionally, it is observed that the natural pH of the reduced matrix is up to 2.5 pH units lower from that of the oxidizing cases, largely in response to H⁺ added through addition of ascorbic acid. It seems that the reduction process by ascorbic acid also effects the matrix polymerization in the presence of Cr. Thus, we conclude that the combination of the reducing agent and the spike chemistry influence the matrix formation. Never the less, although the Cr reduction and spiking affected the geopolymer matrix and caused excessive Si and Al leaching, and a lower natural pH, the overall Cr leaching is still 4-5 time lower that the observed for the oxidized conditions.

Aging affect

In the oxidized Cr samples a significant decrease in the natural pH, of 1.5 pH unit, was observed upon exposure to elevated CO₂ levels (2%), while the air and CO₂ free air condition gave intermediate pH values. This is probably due to the formation of a carbonate-Na species. These changes have not resulted in any significant change in the Cr-leaching behavior of the matrices in the pH dependent leaching test (EPA 1313), probably due to the high solubility and leachability of the Na salt.

On the other hand, the non-oxidized (i.e. 2% CO₂ and N₂ atmospheres) samples leached significantly more Cr in the monolith leaching test (up to 14 wt% EPA 1315) relative to the oxidized ones (up to 8.5%) although no obvious oxidation front was optically observed. This will be further investigated using SEM.

No clear change in the pH pattern was observed for the reduced Cr samples. This is probably due to the relatively low pH imposed by the reducing ascorbic acid (~9.9) that inhibited or limited the precipitation of Na-carbonate salts, and through them an effect on the pH. Even though a reactive front evolution was optically observed in the reduced material under the oxygen bearing aging conditions, the leaching behavior of the material did not vary, thus, indicating that the reacted material is of similar leachability and does not show increased leaching with respect to the material kept under inert condition. The relatively fast reaction rate (a front progress of 1 mm in 60 days) into the material, indicates that a oxidation reaction has significantly affected the material and it can be expected that longer reaction times will induce high leachability to the upper boundary presented by the oxidized Cr samples.

Cr (VI) is highly soluble in water (73 g/100 mL at 25 °C), thus its extreme leaching into the solution could be expected. However, reduced Cr (III) in the form of Cr(OH)₃, expected for reduction by ascorbic acid, is insoluble in water, and behaves as an amphoteric substance (see Eq 1). The constant level of Cr leaching from the reduced samples, observed over the full pH spectrum analyzed, may indicate that either, in spite of the high access of ascorbic acid applied, the high pH in the system prevented full reduction of the Cr and some Cr (VI) remained in the system and leached throughout the pH range, or that the Cr formed upon reduction another less stable mineral or amorphous form, that was more available for leaching.

In summary, under the studied condition this particular formulation has not been found to be sufficiently retentive of Cr either in reduced or oxidized state. More research into types of formulation and reductive agents needs to be done.

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