

Fe speciation in geopolymers with Si/Al molar ratio of ~ 2

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Abstract

The speciation of Fe was studied in metakaolin-based geopolymers to which Fe was added as ferric nitrate solution or freshly precipitated ferric hydroxide. From Mössbauer and near-edge X-ray absorption spectroscopies, coupled with X-ray diffraction and electron microscopy, it was concluded that in as-cured geopolymers the Fe was present in octahedral sites, either as isolated ions in the geopolymer matrix or as oxyhydroxide aggregates which had not reacted with the starting geopolymer components. For material to which iron nitrate was added, heating to 900 °C allowed the formation of nepheline and a glass, both of which contained tetrahedrally coordinated, substituted Fe³⁺.

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1. Introduction

Geopolymers (GPs) with Si/Al molar ratios of ~ 2 are alkali aluminosilicate materials^{1,2} which can be made at near ambient temperatures and are X-ray amorphous. They are composed of cross-linked [AlO₄][−] and [SiO₄] tetrahedra, with charge balancing Na⁺ or K⁺ ions. They are made by exposing reactive aluminosilicate precursors such as fly ash, blast furnace slags or metakaolin (MK) to alkali solutions, with or without silicate, with minimum water addition to make a stiff paste. The mixtures polymerise and solidify upon curing at 20–90 °C, preferably in high humidity and sealed conditions. Their main potential applications are as building materials and a limited number of buildings have been constructed.³ Geopolymers are very heat-resistant compared with Portland cement and also have the potential capability to incorporate and immobilise a variety of radioactive waste ions, including Sr and Cs,^{4–7} as well as mining waste which invariably consists of various minerals containing Ti, Mn, Fe and Ca among many others.^{8,9} A brief overview has been reported on the speciation of these elements in GPs.¹⁰

Iron can be a major component of mining wastes and it can exist in many forms, but it would be more likely to affect the

kinetics and overall chemistry of geopolymer formation if the iron was in a relatively soluble form. As part of this approach, the speciation of iron in an MK-based geopolymer has been studied in some detail in the present work. The basic approach taken was to introduce ferric iron, either as a soluble salt or as freshly precipitated (oxy)hydroxide, to maximise the potential mobility of the Fe in the wet preparation.

2. Experimental

GPs having Si/Al and Na/Al molar ratios of 2.0 and 1.0, respectively were prepared with the necessary additives as listed in Table 1. The molar ratio of water to sodium was 7.2:1. The ferric (oxy)hydroxide was freshly prepared by adding NaOH solution to a solution of Fe(NO₃)₃·9H₂O; the precipitate was filtered and washed with deionised water five times to remove sodium nitrate. The expected product should be either ferrihydrite, Fe₅HO₈·4H₂O, or goethite, α -FeOOH, depending on the speed of reaction.¹¹ The dried precipitate was analysed by powder X-ray diffraction (XRD, see below) and the pattern was very diffuse, but in basic agreement with that of a two-line ferrihydrite pattern.¹²

The (oxy)hydroxide or the nitrate solution was mixed well with the MK in a pestle and mortar for about 10 min before adding to the solution of sodium silicate and water. After mixing for 5 min, the slurry was poured into a 40 mm polycarbonate

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Table 1
Composition of the baseline composition and the additives

Precursor	Mass%
Sodium silicate solution (Type D, PQ Corporation, Australia)—14.7 Na ₂ O, 29.4 SiO ₂ , 55.9 H ₂ O (mass%)	63.0
Metakaolin (heated Kingwhite clay, Unimin Australia Ltd., at 750 °C for 15 h)	33.7
Extra deionised water	3.3
Fe(OH) ₃ —freshly prepared (for details see the text)	1 and 5 ^a
Fe(NO ₃) ₃ ·9H ₂ O (Sigma–Aldrich Australia Ltd.)	1 ^a

^a Added to 100% baseline composition as equivalent Fe₂O₃.

cylindrical jar and covered with a screw cap. This was shaken for 5 min on a vibrating table to de-air. Each batch weighed ~20 g and had dimensions of ~40 mm diameter × 10 mm thick. They were cured at ambient for 24 h followed by curing at 60 °C for 24 h (closed container) and removed from the jar after 3 days. All the GPs were older than 7 days when subjected to further experimentation, to maximise the chances of complete polymerisation.

The samples to which the ferric nitrate was added were heated in air to 600, 700, 800 and 900 °C for 2 h in an electric furnace. Heating and cooling rates were 5 °C/min.

All samples were analysed by XRD (Model D500, Siemens, Karlsruhe, Germany) using Co K α radiation on crushed portions of material. Selected samples were cross sectioned, mounted in epoxy resin, and polished to a 0.25 μ m diamond finish and examined by scanning electron microscopy (SEM: Model 6400, JEOL, Tokyo, Japan) operated at 15 kV and fitted with an X-ray microanalysis system (EDS: Model: Voyager IV, Tracor Northern, Middleton, WI, USA).

Transmission electron microscopy (TEM) and EDS analysis were performed using a JEM 2000fxII (JEOL, Japan) machine with a LaB₆ electron source operated at 200 kV. The TEM was equipped with a LINK energy dispersive X-ray spectrometer and ISIS microanalysis system (both from Oxford Instruments, UK). The Cliff–Lorimer method¹³ was used to analyse energy dispersive spectra with experimental correction factors determined from a suite of natural mineral and synthetic ceramic materials of known composition. A Model 636 double tilt liquid nitrogen cooled specimen holder and a Model 613-0500 cold stage controller (both from Gatan, USA) were used for TEM/EDS analyses.

Care was taken to minimise electron beam damage during EDS analyses by cooling the sample to liquid nitrogen temperature and by ensuring the electron beam was never focussed below 200 nm diameter. Despite these precautions the measured sodium content was significantly lower than expected, most likely due to Na migration caused by the electron beam.

X-ray absorption near-edge structure (XANES) measurements were carried out at beamline 24A, National Synchrotron Radiation Research Centre (NSRRC), Hsinchu, Taiwan.¹⁴ The powdered samples were spread on double-sided copper tape and mounted on a stainless steel sample holder. Fe L-edge X-ray absorption spectra were taken in the total-electron yield (TEY) mode by monitoring the specimen current.

Mössbauer spectroscopic analysis of the iron phases was carried out at room temperature using a conventional constant acceleration drive and a ⁵⁷CoRh source. Velocity calibration was carried out with α -Fe and all isomer shifts are quoted relative to α -Fe at room temperature. Fitting was carried out by conventional least squares techniques, with the intensities and linewidths of doublet lines, and also the corresponding lines of sextets, constrained to be equal. In the sextet fitting, it was also assumed that the hyperfine field and the electric field gradient were collinear.

3. Results and discussion

3.1. X-ray diffraction

Table 2 lists XRD analyses for all the GPs made, including the heating results and the sample to which iron nitrate was added. The XRD traces of all GPs indicated the presence of an amorphous phase by the broad diffuse peak centred at ~0.32 nm (see Fig. 1), together with weak peaks due to crystalline anatase and quartz impurities in the MK, as observed by other workers on MK-based geopolymers.¹⁵ These impurities in the original clay were estimated at ~1 mass% (see Figs. 1 and 2).

When Fe is added as the (stable) nitrate to the geopolymer mixture, Fe (oxy)hydroxide would likely precipitate in

Table 2
XRD analyses of heated and unheated GPs

Equivalent Fe ₂ O ₃ equivalent additions to GPs (mass%)	Heat treatment (°C)	XRD analysis
1 (hydroxide)	22	Am (M), Q (m), A (m)
5 (hydroxide)	22	Am (M), Q (m), A (m), iron hydroxide (m)
1 (nitrate)	22	Am (M), Q (m), A (m), NaNO ₃ (m)
1 (nitrate)	600	Am (M), Q (m), A (m)
1 (nitrate)	700	Am (M), Q (tr), A (tr)
1 (nitrate) ^a	800	Am (M), N (m), A (tr)
1 (nitrate) ^a	900	N (M), Am (m)

Am, amorphous; Q, quartz; A, anatase; N, nepheline; M, major; m, minor; tr, trace.

^a 1 and 5 mass% of hydroxide when heated showed N (M) and Am (m) as phases.

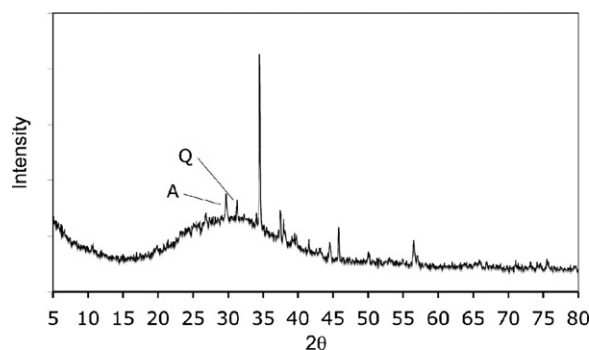


Fig. 1. XRD trace of unheated GP, containing 1 mass% equivalent Fe₂O₃ added as the nitrate (A, anatase; Q, quartz; rest, NaNO₃ peaks).

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