

KU LEUVEN

Proceedings of the
THIRD INTERNATIONAL

SLAG VALORISATION SYMPOSIUM

THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

19-20 March 2013
Leuven, Belgium

Editors Annelies Malfliet, Peter Tom Jones, Koen Binnemans, Özlem Cizer, Jan Fransaer, Pengcheng Yan, Yiannis Pontikes, Muxing Guo, Bart Blanpain



GLASS REACTIVITY: ANALYSIS BY DISSOLUTION EXPERIMENTS

Ruben SNELLINGS¹, Karen SCRIVENER¹

¹ Laboratory of Construction Materials, EPFL, 1015 Ecublens, Switzerland

ruben.snellings@epfl.ch, karen.scrivener@epfl.ch

Abstract

This paper introduces dissolution experiments at high pH and high solution undersaturation as a promising analytical technique to directly study the reactivity of glasses and other inorganic materials. Dissolution rates were measured of a series of synthetic calcium aluminosilicate glasses ranging in composition from blast-furnace slag to silica fume. Both the glass and the solution composition exert a strong effect on the measured dissolution rates. Glasses containing an excess amount of Ca as framework modifier show dissolution rates an order of magnitude higher than that of the tectosilicate glasses in which Ca charge balances the substitution of Al for Si in the framework. Addition of Al in solution has a strongly retarding effect on the dissolution of tectosilicate glasses, but not on the dissolution of high-Ca depolymerised glasses.

Introduction

The reuse of high temperature residues as supplementary cementitious materials (SCMs) in blended cements represents one of the most effective ways of reducing the environmental impact of cement production. One of the major limiting factors on SCM levels in blended cements is the lowered early compressive strength. In consequence, enhancing the reactivity of slags and fly ashes is a key to further reducing clinker factors in blended cements.

The reactivity of aluminosilicate glasses in blended cements has been linked to their chemical composition. However, the relationship between normative hydraulic indices and compressive strength are very roughly defined and do not allow an accurate prediction of compressive strength.

As the hydration of blended cements can be considered as a series of coupled reactions involving dissolution of reactants and precipitation of products, analysis of the reaction kinetics as individual steps is instrumental in delivering a more fundamental understanding. In this paper, the reactivity of synthetic glasses covering the compositional range from blast-furnace slags over fly ashes to silica fume is tested using dissolution experiments at high pH.

Materials and methods

Calcium aluminosilicate glasses were synthesised from mixtures of reagent grade Al_2O_3 , CaCO_3 and SiO_2 at 1600°C . The samples were water-quenched.

The sample preparation for the dissolution experiments consisted hand grinding and sieving to obtain the 50-125 μm fraction. This fraction was repeatedly cleaned ultrasonically to remove surface adsorbed particles. The particle size distribution was measured by laser diffraction and the specific surface area was measured by the five-point BET method. X-ray powder diffraction analysis was used to check whether any crystalline phases were present in the glasses. Glass samples were studied by Scanning Electron Microscopy (SEM) using a SFEG XL 30.

The dissolution experiments were carried out in batch reactors. In this system, the dissolution rate is calculated from the measured increase in solution concentration of the glass components. Dissolution experiments were performed at 20°C , a water:glass ratio of 1000, pH of 13, and variable initial Al concentrations of 0, 0.25, 1 and 5 mM Al. The solutions were prepared using ultrapure water (resistivity $>18 \text{ M}\Omega \text{ cm}$), analytical grade NaOH and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Ca, Al and Si solution concentrations were measured by ICP-OES using matrix-matched standard solutions.

Table 1: Properties of model glasses for blast-furnace slag (BFS), fly ash (FA), natural pozzolan (NP) and silica fume (SF)

Glass type		Chemical composition (wt%)			BET (m^2/g)	Grain size d_{50} (μm)
		CaO	Al_2O_3	SiO_2		
G1	BFS	43.0	19.0	38.0	0.0091	114.7
G2	BFS	36.0	16.0	48.0	0.0151	107.2
G3	FA	20.0	37.0	43.0	0.1004	116.0
G4	FA	15.0	27.0	58.0	0.0501	113.2
G5	NP	6.5	11.5	82.0	0.0548	115.2
G6	SF	0.0	0.0	100.0	0.0440	107.1

Results

Glass synthesis and characterisation

The selected glass compositions simulate the compositional range of glasses encountered in SCMs in terms of Ca, Al and Si content (Table 1). The melting and quenching process was considered successful based on the absence of Bragg peaks in the powder XRDs. The effect of the changing composition on the glass structure is clearly visible in the shift of the diffuse scattering maximum from 3 \AA to 4.15 \AA for G1 to G6, respectively. All samples show very similar particle size distributions (Table 1), particles

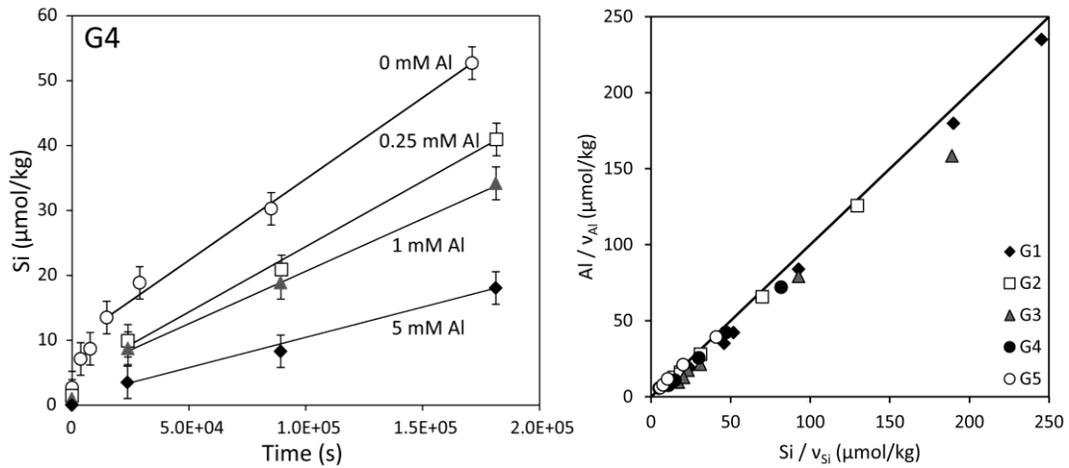


Figure 1: Increase in Si concentrations during dissolution of G4 in solutions with varying initial Al concentrations (left); normalised Al vs. Si plot showing the congruency of dissolution at high undersaturations, avoiding product precipitation

larger than $125 \mu\text{m}$ were detected by both laser granulometry and SEM as sieving imposes a hard limit only on the smallest particle diameter. The BET specific surface varies to a larger extent, possibly indicating differences in roughness of the glass surfaces. The particles of the sieved and cleaned glass samples are sharp-edged and show smooth, fresh surfaces.

Glass dissolution kinetics

The batch dissolution experiments show an initially non-linear increase of Si concentration in time, corresponding to a non-steady state dissolution regime (Figure 1). It is assumed here that the subsequent linear concentration increase represents a steady-state dissolution regime and that the derived dissolution rates correspond to steady-state dissolution rates. A plot of Al to Si concentrations normalised to their respective fraction in the glass (v_{Al} or v_{Si}) clearly illustrates that glass dissolution at highly undersaturated, high pH conditions is congruent. No significant preferential release of Al or Si can be observed.

The glass dissolution rates are the highest for the BFS type glasses, and decrease with decreasing Ca and Al contents (Figure 2). This is explained by differences in the polymerisation of the glass structure. If more Ca is present than needed for charge balancing the replacement of Al for Si in the Q^4 network, the aluminosilicate framework will be more depolymerised and the glass will dissolve faster¹. Figure 2 also shows the effect of the presence of Al in solution on the glass dissolution rate. Al has been demonstrated to slow down the dissolution of aluminosilicate minerals and glasses significantly². Interestingly, this inhibitory effect is observed to act on all tectosilicate (Q^4) glasses, the effect being stronger for Al-poor glasses. To the contrary, Al in solution appears to have only a negligible or limited effect on the dissolution of BFS type glasses.

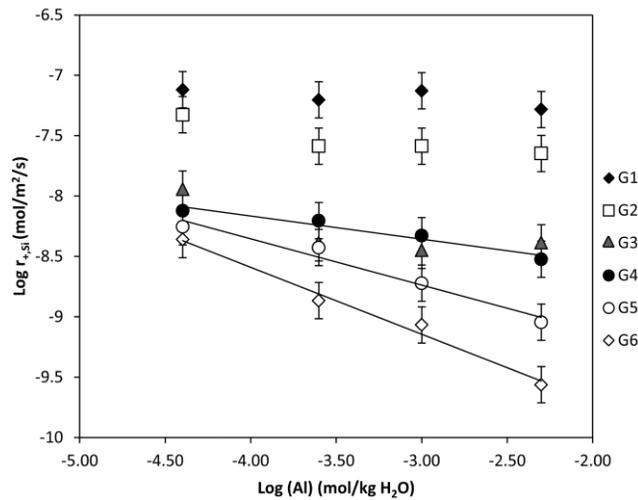


Figure 2: Effect of Al concentrations in solution on glass dissolution rates at pH 13. The dissolution of tectosilicate glasses is strongly retarded by the presence of Al in solution

Conclusions

The presented paper demonstrates the analytical potential of dissolution experiments to test and study the reactivity of glasses and, in extension, supplementary cementitious materials. The effect of solution composition on the dissolution kinetics is illustrated by the results showing the inhibitory effect of Al in solution on the dissolution rates of tectosilicate glasses.

Acknowledgements

Financial support by the FP7-Marie Curie IEF grant 298337 is gratefully acknowledged.

References

1. E. Olbrich and G.H. Frischat, "Corrosion of granulated blast furnace slags in aqueous solutions", *Glastech. Ber. Glass Sci. Technol.*, **74** (4) 86-96 (2001).
2. E.H. Oelkers, "General kinetic description of multioxide silicate mineral and glass dissolution", *Geochim. Cosmochim. Acta*, **65** 3703-19 (2001).