Glass reactivity: analysis by dissolution experiments

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ABSTRACT

At pH 13, glass dissolution rates were observed to scale linearly with the glass Ca/(Al+Si) molar ratio. Ca-rich blast-furnace type glass dissolution was shown to be up to one order of magnitude faster than tectosilicate fly ash and silica fume type glass dissolution, supporting different pathways to dissolution. In solutions that are strongly undersaturated with respect to hydrous glass and hydration products, glass dissolution rates are independent of changes in solution undersaturation and aqueous Si activity. In contrast, dissolution rates decrease with aqueous Al concentration for tectosilicate type glasses. The insights gained are instrumental in finding ways to enhance the reactivity of supplementary cementitious materials (SCMs).

INTRODUCTION

Supplementary cementitious materials (SCMs) are widely used to partially replace Portland clinker in blended cements. Reducing clinker contents further without compromising the development of early strength necessitates a better assessment and enhancement of the reactivity of the available SCMs. To this purpose the reactivity of synthesized calcium aluminosilicate glasses covering a compositional range from blast-furnace slags over fly ashes to silica fume was analyzed by dissolution experiments. Initial glass dissolution rates were measured at 20°C and pH = 13, and with varying initial concentrations of aqueous Al and Si.

METHODS AND MATERIALS

Calcium aluminosilicate glasses were synthesized from mixtures of reagent grade Al_2O_3, $CaCO_3$ and SiO_2 at 1600 °C (Figure 1). The samples were water-quenched. The 50-125 µm fraction was used in the dissolution experiments. 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.

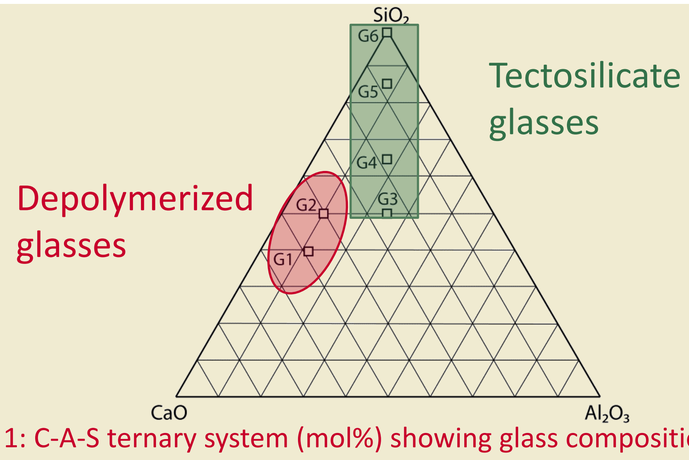

Fig. 1: C-A-S ternary system (mol%) showing glass compositions

Glass composition controlled dissolution

The glass dissolution rates are highest for blast-furnace slag type glasses, and decrease with decreasing Ca and Al contents (Figure 2). This is explained by differences in the polymerization 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 depolymerized and the glass will dissolve faster.

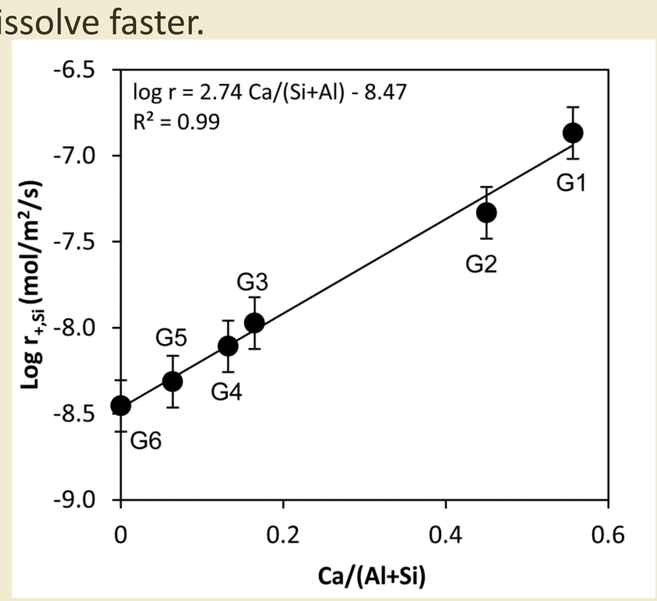

Fig. 2: Variation of the logarithm of the dissolution rates with the Ca/(Al+Si) molar ratio of the glasses

Solution controlled dissolution

Figure 3 shows the effect of the presence of Al in solution on the glass dissolution rate. An inhibitory effect of aqueous Al is observed to act on all tectosilicate 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.

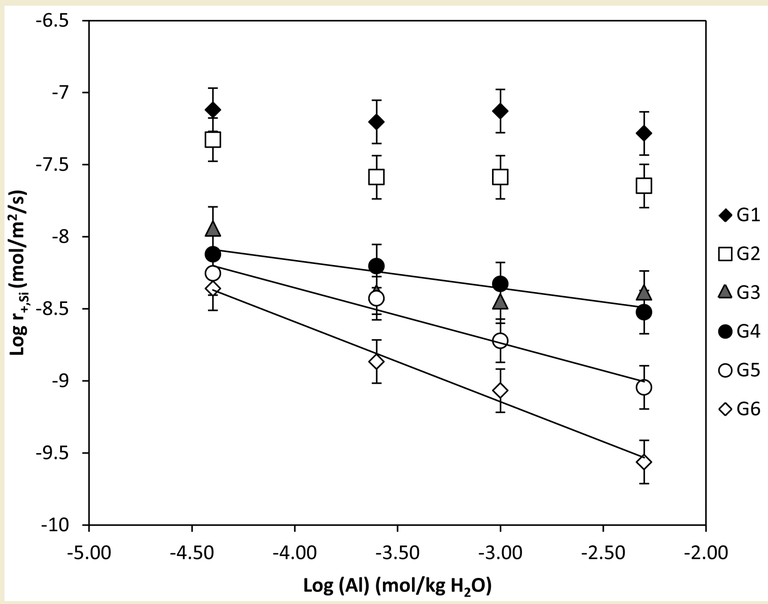

Fig. 3: Logarithm of the glass dissolution rates as a function of total aqueous Al concentration

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CONCLUSIONS

- ✓ Dissolution rates correlate with the glass Ca/(Al+Si) ratio, dissolution rates of depolymerized glass are up to one order magnitude higher than tectosilicate glass.
- ✓ Aqueous Al exerts a strong inhibitory effect on the dissolution of tectosilicate glasses.

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