Investigations of introducing manganese into brownmillerite

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Abstract. Solid solution series of manganese brownmillerites and different oxygen defect perovskites were characterised in the system Ca$_2$Fe$_2$O$_5$ (C$_2$F) - “Ca$_2$Mn$_2$O$_5$” (“C$_2$Mn”) - “Ca$_2$Al$_2$O$_5$” (“C$_2$A”). Samples were synthesised by solid state reactions in a temperature range of 1250-1300°C. The stability fields of different phases were investigated by powder X-ray diffraction. The corresponding d-spacings were determined. Ternary solid solutions of hydraulic brownmillerites crystallise in a range of 2CaO (1-x) Fe$_2$O$_3$ (0.5-y) Mn$_2$O$_3$ (0.66-z) Al$_2$O$_3$ (0 > x < 1; 0 < y < 0.5; 0 < z < 0.66; x + y + z = 1). First investigations have shown that a replacement of 25 mol-% iron by manganese in the brownmillerite structure leads to an increase of hydraulic properties.

Introduction

Manganese containing High Alumina Cements were performed by addition of manganese bearing materials (manganese ore, manganese remnants) to raw materials of HAC [1]. Lowered production temperatures and lower costs of raw material lead to a highly reactive cement. Depending on the composition of the raw materials and the clinkering conditions different new phases can be formed. Generally manganese solid solutions with brownmillerite and monocalciumaluminate and other cement mineral phases can crystallise. The brownmillerite phase in cements acts as a host and scavenger for many elements present in cement. The addition of manganese to cement raw materials increases the compositional range of the brownmillerite phase. Ratio and composition of the brownmillerite phase are influence to the hydraulic character of cement. The investigations to the phase formation in the Ca$_2$Fe$_2$O$_5$-“Ca$_2$Mn$_2$O$_5$-“Ca$_2$Al$_2$O$_5$” system were performed to establish the stability limits of brownmillerite phases for creation of manganese containing high alumina cement. Furthermore, it was necessary to determine X-ray powder data of pure brownmillerite and perovskite phases to establish identification possibilities in cementitious systems.
Phase stability of Brownmillerite and Perovskite of the system

\[ \text{Ca}_2\text{Fe}_2\text{O}_5 \ (\text{C}_2\text{F}) - \text{“Ca}_2\text{Mn}_2\text{O}_5” \ (\text{“C}_2\text{Mn”}) - \text{“Ca}_2\text{Al}_2\text{O}_5” \ (\text{“C}_2\text{A”}) \]

The crystal structure of brownmillerite is related to the perovskite one. The ideal \( \text{A}_2\text{B}_2\text{O}_6 \)-perovskite structure consists of layers of corner sharing \( \text{BO}_6 \)-octahedra with calcium atoms in between. The \( \text{A}^{2+}\text{B}^{3+}_2\text{O}_5 \)-brownmillerite structure can be described as a perovskite structure with one-sixth of the anion sites vacant. The oxygen vacancies lead to a structure which is composed of alternating layers of corner sharing \( \text{BO}_6 \)-octahedra and \( \text{BO}_4 \)-tetrahedra zig-zagly arranged along the b-axis. The calcium atoms are located in the open spaces in between. The structures of perovskite and brownmillerite are illustrated at Figure 1.

In order to characterize manganese substituted brownmillerite solid solutions and to determine their stability range, Mn-substituted batches were synthesised by heating a mixture of \( \text{CaCO}_3, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3 \) and \( \text{MnO}_2 \) for 48-120h at temperatures between 1250-1300°C. The sintered powders were analysed by X-ray diffraction analysis (Siemens D5000). Lattice parameters of all samples were determined. In the \( \text{Ca}_2\text{Fe}_2\text{O}_5 \)-,\( \text{Ca}_2\text{Mn}_2\text{O}_5 \)-,\( \text{Ca}_2\text{Al}_2\text{O}_5 \)-system \( \text{Fe}^{3+} \) was replaced by \( \text{Mn}^{3+} \) in the crystalline structure of calciumferrites and \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) by \( \text{Mn}^{3+} \) in calciumaluminateferrites.

![Fig. 1: Schematic structures of a brownmillerite (left) and perovskite (right). The crystal structure of \( \text{A}^{2+}\text{B}^{3+}_2\text{O}_5 \)-brownmillerite \((\text{A} = \text{Ca}^{2+}; \text{B} = \text{Al}^{3+}, \text{Mn}^{3+}, \text{Fe}^{3+})\), an oxygen-deficient perovskite type, consists of alternating layers of corner sharing \( \text{BO}_6 \)-octahedra and \( \text{BO}_4 \)-tetrahedra. The perovskite structure \( \text{A}^{2+}\text{B}^{4+}_2\text{O}_6 \)-(A = Ca\( ^{2+} \); B = Mn\( ^{4+} \), Fe\( ^{4+} \)) composed of alternating layers of corner sharing \( \text{BO}_6 \)-octahedra. The \( \text{A}^{2+} \)-ions located in the open spaces in-between are not shown. The modified Figure is described by [2].](image)
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The phase relations in the pseudo-ternary system $\text{Ca}_2\text{Fe}_2\text{O}_5$-"$\text{Ca}_2\text{Mn}_2\text{O}_5$"-"$\text{Ca}_2\text{Al}_2\text{O}_5$" are shown in Figure 2 [3]. Hydraulic solid solutions of brownmillerite structure type are crystallising with varying contents of iron, manganese and aluminium in area A ($\text{C}_2\text{F}$-$\text{C}_6\text{A}_2\text{F}$-$\text{C}_4\text{A}_2\text{Mn}$-$\text{C}_6\text{AMn}$-$\text{C}_6\text{A}_0.5\text{FMn}$-$\text{C}_2\text{F}_0.83\text{Mn}_0.17$). Brownmillerite, $\text{C}_2\text{A}_7$ and $\text{C}_3\text{A}$ coexist in field B. Different oxygen defect perovskites are stable in area C. "$\text{C}_2\text{Mn}$" crystallises as $\text{CaMnO}_{2.8}$ and "$\text{C}_4\text{FMn}$" as $\text{CaFe}_{0.5}\text{Mn}_{0.5}\text{O}_{3-x}$. In Fields D, E, and F coexist brownmillerite-type solid solutions and different oxygen defect perovskites, depending on the amount of Manganese and the conditions. The stoichiometry of the oxygen defect perovskites structure "$\text{C}_2\text{Mn}$" was determined using TPR-measurements with $\text{CaMn}_{0.60}\text{Mn}_{0.40}\text{O}_{2.8}$. The stability of brownmillerite ($\text{Al}^{3+}$, $\text{Fe}^{3+}$, $\text{Mn}^{3+}$) or perovskites ($\text{Fe}^{3+}$, $\text{Fe}^{4+}$, $\text{Mn}^{4+}$, $\text{Mn}^{3+}$) depend on the clinkering conditions such as temperature range and $pO_2$. The oxidation control of the sintering conditions can play a very important role in avoiding crystallisation of hydraulic brownmillerite or inert perovskite. First investigations showed that a 25 mol% replacement of $\text{Fe}^{3+}$ by $\text{Mn}^{3+}$ in the brownmillerite structure leads to an increase of the hydraulicity properties.

References