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# INVESTIGATIONS ON INTRODUCING Si AND Mg INTO BROWNMILLERITE —A RIETVELD REFINEMENT

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## ABSTRACT

Brownmillerite (commonly $C_4AF$) was synthesized in a laboratory furnace. The product was examined by X-ray powder diffraction and the structure was refined by the Rietveld method. Further syntheses were made under various conditions by substituting $Fe_2O_3$ by MgO + $SiO_2$ according to the formula $C_4AF_{1-x}M_xS_x$. All samples were examined by X-ray diffraction and quantified by Rietveld method due to their content of Brownmillerite, $C_2S$ and MgO. All results show that the whole $SiO_2$ content could be calculated as $C_2S$. MgO could be partially found as periclase. Brownmillerite shows a shift of lattice parameters according to the solid solution series $C_6A_2F$ - $C_2F$.

## Introduction

Brownmillerite is one of the four main components in ordinary Portland cement. The chemical composition is mainly based on microprobe investigations and chemical analysis of separated materials([1],[2],[3],[4],[5],[6],[7]). Table 1 shows the average composition of Brownmillerite given by [8].

Own investigations should proof the introduction of $Fe_2O_3$ by MgO and $SiO_2$ into the crystal structure of Brownmillerite. Refinement of the Brownmillerite structure [9] by the Rietveld method should give information about the atomic positions of Mg and Si.

## Methods

All syntheses were made from pure components using the following reagent grade chemicals:

- CaO
- MgO
- low - Quarz
- $\gamma$-$Al_2O_3$
- $Fe_2O_3$

TABLE 1

Chemical Composition of Brownmillerite According to [8] (values in wt.%)

| $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $TiO_2$ | $Mn_2O_3$ | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| 0,1 | 3,0 | 21,9 | 3,6 | 0,2 | 47,5 | 1,6 | 0,7 | 21,4 |

All mixtures were pulverized in a disc mill. The samples were fired in a temperature range of 1150°C - 1300°C and were air quenched afterwards. X-ray investigations were made on a Siemens D5000 powder diffractometer with the following parameters.

Generator: 30 mA, 40 kV
Radiation: Cu Kα
Filter: Ni
Diffractometer:
Bragg-Brentano geometry

Continuous scan: 0,02 °2Θ/4s
Fixed slits: 0,5°
Detector slit: 0,1°
Detector: Scintillation

Rietveld refinement was done with the modified software of Wiles and Young. Five compounds (structure data in brackets) which were present in ordinary Portland cement were quantified in the synthetic samples:

Alite [10]
Belite [11]
$C_3A$ [12]
Brownmillerite [9]
Periclase

All structure data had been refined using pure phases.

## Results

The chemical compositions of synthesized mixtures are given in table 2. All mixtures were fired at 1150°C for 15 hours interrupted two times for grinding. The mixture with the composition $C_4AF_{0,7}M_{0,3}S_{0,3}$ was also fired at 1250°C and 1300°C. Figure 1 shows observed and calculated X-ray pattern of $C_4AF$.

TABLE 2

Chemical composition of synthesized samples

| Formula | CaO | $Al_2O_3$ | $Fe_2O_3$ | MgO | $SiO_2$ |
|---|---|---|---|---|---|
| $C_4AF$ | 46,2 | 21,0 | 32,8 | - | - |
| $C_4AF_{0,7}M_{0,3}S_{0,3}$ | 47,9 | 21,8 | 23,9 | 2,6 | 3,8 |
| $C_4AF_{0,6}M_{0,4}S_{0,4}$ | 48,5 | 22,1 | 20,7 | 3,5 | 5,2 |

all values in wt.%

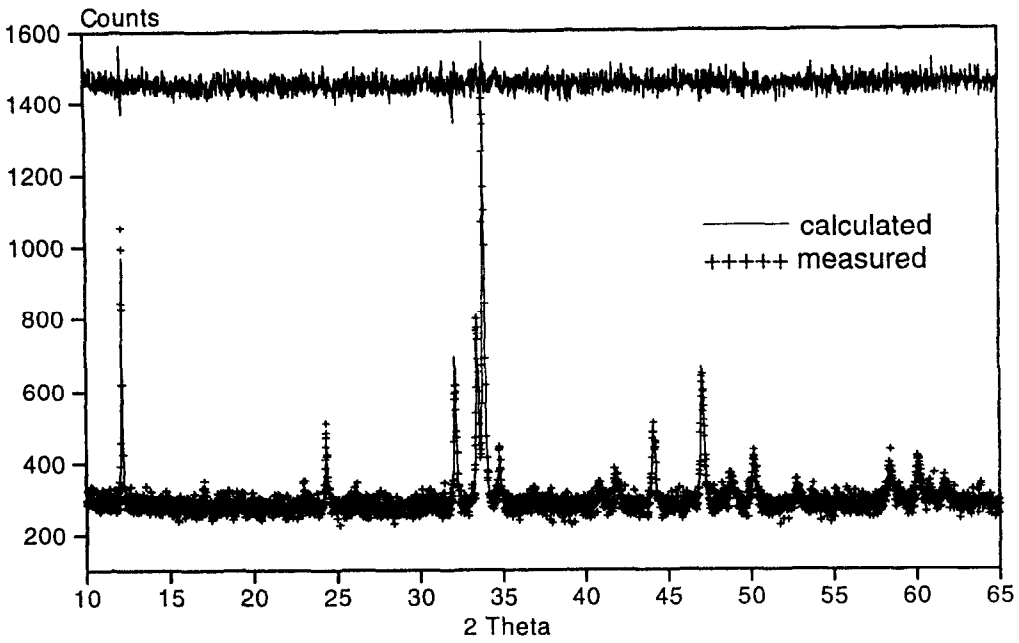


FIG. 1.
Observed and calculated X-ray pattern of C4AF including difference plot.

The residual errors are summarized in table 3. Table 4 shows the result of the quantification by Rietveld full profile refinement.

Nor Alite neither $C_3A$ can be detected in the mixtures. The sample which was fired at 1300°C melted completely so no phase distribution could be calculated. The refined lattice parameters of Brownmillerite shows shifts within the solid solution series of $C_6A_2F$-$C_2F$ to aluminate enriched members [13]. Table 5 shows the comparison of lattice parameters of ferrite phases from the solid solution series $C_6A_2F$-$C_2F$ and ferrite phases obtained from the synthesized mixtures containing MgO and $SiO_2$. The presence of Belite in Brownmillerite is very difficult to detect. Figure 2 shows a zoomed region of the X-ray pattern of Brownmillerite containing about 15 wt.% Belite.

Figure 3 shows the same zoomed region of Brownmillerite free from Belite.

TABLE 3
Residual Errors of C4AF Refinement

| | R | RwP | Bragg-R |
|---|---|---|---|
| $C_4AF$ | 5,9 | 6,0 | 8,7 |

TABLE 4

Quantification by Rietveld full profile refinement

| Mixture | Brownmillerite calculated by Rv | Periclase calculated by Rv | Belite calculated by Rv | Belite calculated by $SiO_2$ content |
|---|---|---|---|---|
| $C_4AF$ | 100 | 0 | 0 | 0 |
| $C_4AF_{0,7}M_{0,3}S_{0,3}$ | 88,4 | 1,4 | 10,2 | 10,9 |
| $C_4AF_{0,7}M_{0,3}S_{0,3}$ (1250°C) | 87,1 | 2,0 | 10,9 | 10,9 |
| $C_4AF_{0,6}M_{0,4}S_{0,4}$ | 83,0 | 2,4 | 14,6 | 14,9 |

all values in wt.%, Rv = Rietveld refinement, Temperature of syntheses 1150°C

## Conclusion

No introduction of Si into Brownmillerite under above described conditions is possible. The whole $SiO_2$ content of the mixtures can be calculated as Belite. MgO can partially be detected as Periclase. The remaining 20 to 40 % of MgO should be introduced into Brownmillerite and Belite.

Ordinary Portland cement manufactured under realistic technical conditions shows crystallization of Belite in the interstitial phase [14]. Own reflected light microscopy investigations of technical produced clinker confirm this statement. Figure 4 shows Belite in the interstitial phase.

Small dark dots in the brightly shining matrix are small grains of Belite crystallizing in the interstitial phase.

A possible introduction of Si into Brownmillerite during the technical cement manufacturing process leads to metastable Brownmillerites which can exsolve Belite at lower temperatures. Additionally this Belite is very fine grained so that identification is very difficult. Magnesium

TABLE 5

Comparison of the Lattice Parameters of Brownmillerites

| Chemical composition | a in Å | b in Å | c in Å |
|---|---|---|---|
| $C_4AF_{0,7}M_{0,3}S_{0,3}$ | 5,543 | 14,511 | 5,327 |
| $C_{3,4}AF_{0,7}$[13] | 5,542 | 14,507 | 5,328 |
| $C_4AF_{0,6}M_{0,4}S_{0,4}$ | 5,535 | 14,497 | 5,323 |
| $C_{3,2}AF_{0,6}$[13] | 5,534 | 14,496 | 5,321 |
| $C_4AF$ | 5,566 | 14,525 | 5,349 |

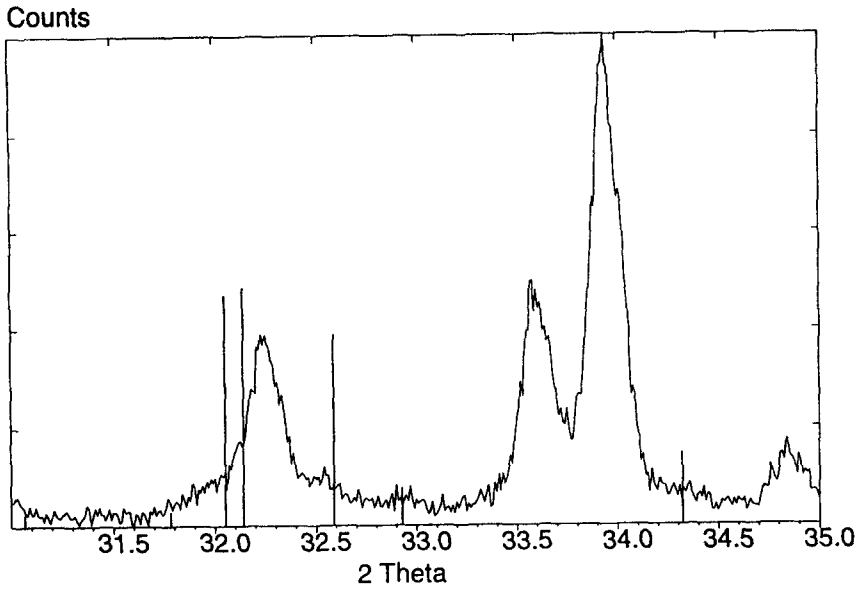


FIG. 2.
Reflections (signed as bars) of 15 % Belite in Brownmillerite (C3.2AF0.6).

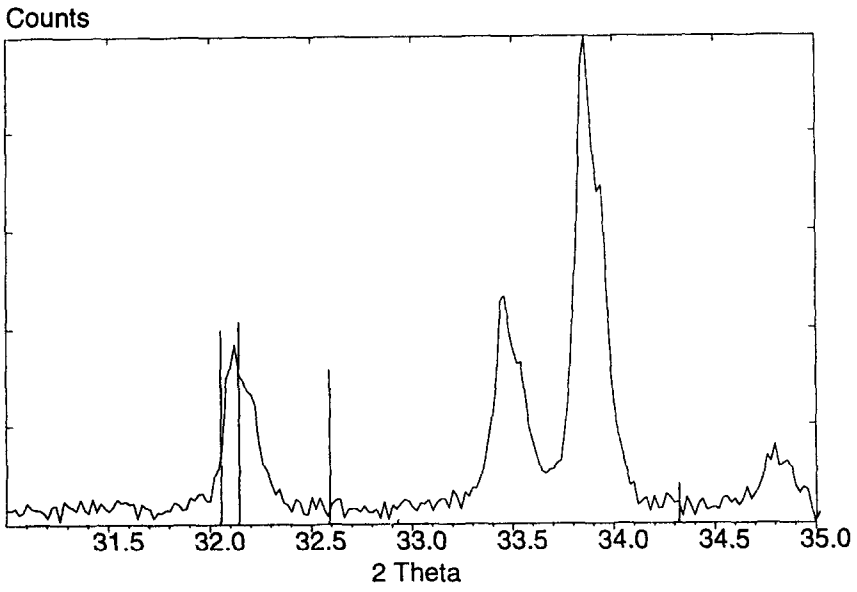


FIG. 3.
X-ray pattern of Brownmillerite (C4AF) free from Belite.

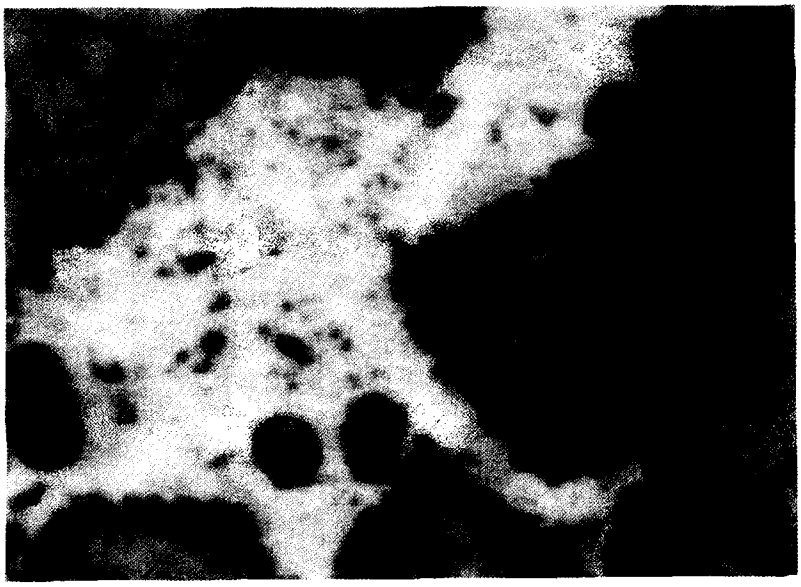

FIG. 4.
Belite crystallized in the interstitial phase (image width 30 μm).

can partially be separated as Periclase. The incorporation of Magnesium into Belite and Brownmillerite can be assumed but the atomic sites where Magnesium can substitute main elements are not yet known.

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