SUPERPARAMAGNETIC BEHAVIOUR OF CEMENT CLINKER AND ITS FERRITE PHASE DOPED WITH DIFFERENT IMPURITIES

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Two oxide mixtures of clinker and its ferrite phase of compositions (66.5 wt.% CaO + 24.5 wt.% SiO_2 + 6.0 wt.% Al_2O_3 + 3.0 wt.% Fe_2O_3) and (60.4 wt.% CaO + 15.4 wt.% Al_2O_3 + 24.2 wt.% Fe_2O_3) respectively were divided into portions and were mixed individually with 0.5, 1, 1.5 or 3 wt.% of LiF, MgF_2, CaF_2, $CaCl_2$ or ZnO. Each portion of clinker was fired at 1450°C and each portion of ferrite was fired at 1350°C for 30 min. *then quenched in air. Mössbauer effect and X-ray diffraction measurements were performed on each sample. The impurities doping produced small particle size. The LiF doping gave the smallest particle size and the highest blocking temperature. The ferrite with LiF exhibited two Fe^{3+} sites while the other used impurities gave one site only. The superparamagnetic relaxation appeared only in the spectra of ferrite with impurities, which means that the impurities in clinker have a tendency to combine with the calcium silicate phases not with C_4AF.*

1. INTRODUCTION

It is well known that cement clinker is composed of four main phases which are: C_2S, C_3S, C_3A and C_4AF (cement nomenclature: C=CaO, S = SiO_2, A = Al_2O_3 and F = Fe_2O_3). These phases are produced from the oxides of calcium, silicon, aluminium and iron which are found naturally in limestone, shale and clay. Due to the presence of other compounds in these raw materials, the produced cement clinker may contain some impurities which affect its clinkering temperature and its characteristics. These impurities may be alkali oxides, fluorides or sulfides, its effect on cement characteristics have been investigated using cement clinker or one of its four main phases /1-6/.

The presence of fluorides influences both the mechanism of formation of C_3S and of C_2S in the cement clinker. As CaF_2 doping in cement clinker was increased /5/ the phase C_3A is gradually replaced by the phase $C_{11}A_7.CaF_2$, while the β- to γ-C_2S polymorphic transition is enhanced and the average particle size of the clinker minerals decreases. Only a small amount of the fluorine added to the raw meal is lost in the firing process /5/ while the remainder fraction is preferentially concentrated in the $C_{11}A_7.CaF_2$ phase. However a significant amount of CaF_2 is also taken up by the calcium silicates, specially in the absence of $C_{11}A_7.CaF_2$. Where the A/F ratio of the phase $C_2(A,F)$ is shifted to higher values with increasing fluorine content in the clinker.

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The effect of ZnO doping on the structure of portland cement clinker show the same features as CaF_2 doping in clinker /6/.

This work is concerned with the effect of halogen ions or ZnO addition to cement clinker or its ferrite phase on their particle size, and on their superparamagnetic behaviour using X-ray diffraction and Mössbauer spectrometry, in order to explore more informations about the iron ions in C_4AF phase and the clinker.

2. EXPERIMENTAL

The pure cement clinker was prepared according to the composition /5, 6/ (66.5 wt.% CaO + 24.5 wt.% SiO_2 + 6.0 wt.% Al_2O_3 + 3.0 wt.% Fe_2O_3). The pure ferrite phase C_4AF of cement clinker was also prepared as (60.4 wt.% CaO + 15.4 wt.% Al_2O_3 + 24.2 wt.% Fe_2O_3). A portion from each base mixture was left pure and the remainder portion of each mixture was divided into several portions. Impurities such as LiF, MgF_2, CaF_2, $CaCl_2$ or ZnO were added by the percentages of 0.5, 1.0, 1.5 or 3 wt.% to each portion individually. All chemicals used were of high purity grade. Pellets made from these raw meals were placed into Pt dishes, fired for 30 min. at 1450°C for clinker mixtures and at 1350°C for ferrite mixtures in an electric oven and rapidly cooled in air.

All samples were grounded and measured by X-ray diffraction (XRD) at room temperature (R.T.) and by Mössbauer spectroscopy (MS) at different tmperatures. The XRD measurements were done using CuKα radiation. MS measurements were performed using a velocity drive in constant acceleration mode. The calibration was done with an iron foil of natural abundance and a source of Co-57 in Pd matrix was used.

3. RESULTS AND DISCUSSIONS

3.1. XRD data

3.1.1. XRD data of the cement clinker

The XRD peaks of pure clinker shown in Fig. 1a., are observed also in the other clinker patterns with some changes in their intensities. Where as the impurities content was increased the β- to γ-C_2S polymorphic transition increased, while the C_3A phase and C_3S phase content decreased.

From XRD patterns of Fig. 1. the particle size /7/ of the clinker minerals decreased with increasing the impurities content. In clinker ZnO was preferentially concentrated in the interstitial phase /6/, accompanying Al_2O_3 and Fe_2O_3, even though a significant fraction of the total Zn ions replaced Ca ions in the crystalline lattice of clinker minerals /6/. Halogen ions in clinker were not evenly distributed between the interstitial phase and the calcium silicates /5/.

3.1.2. XRD data of the ferrite phase

All the XRD peaks characterizing the ferrite phase of cement clinker are present as shown in Fig. 2. As the impurities content increased the intensity of the $2\theta = 33.2^\circ$ peak increased while the intensity of that at $2\theta = 33.5^\circ$ decreased. This means that the impurities ions are preferentially located in the interstitial sites

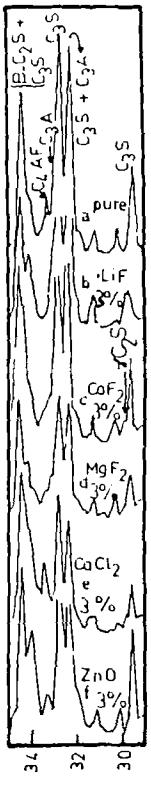

Fig.1.
Representative XRD patterns of C_4AF with and without impurities.

Fig.2.
Representative XRD patterns of C_4AF with and without impurities as indicated in Fig.1.

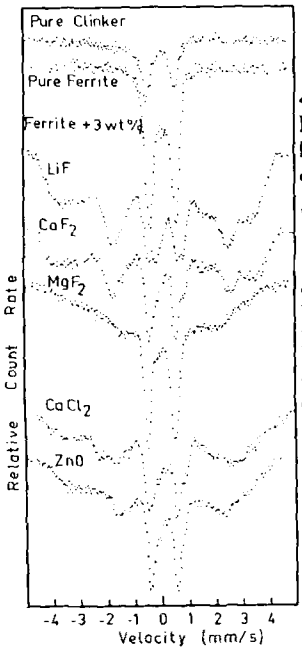

Fig. 3. Representative Mössbauer spectra of pure clinker, and C_4AF with and without impurities as indicated.

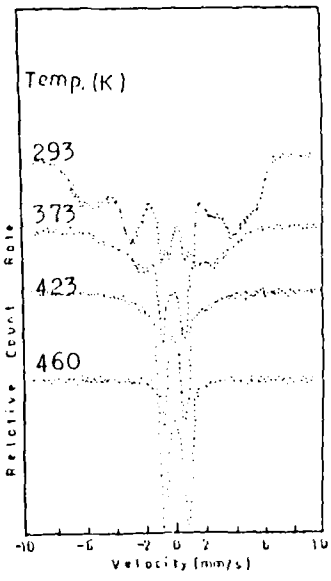

Fig. 4. Representative Mössbauer spectra of C_4AF doped with 3.0 wt.% LiF at different temperatures.

of C_4AF /4/. If the sample was quenched the presence of impurities in the C_4AF mixture may cause minimization of the particle size of C_4AF.

The particle size of C_4AF phase was found /7/ with a minimum value (40 Å) for LiF and CaF_2 addition. This value increased gradually in the range 70-100 Å when $CaCl_2$, MgF_2 or ZnO was added. However, for pure C_4AF the particle size is larger than 100 Å, so no magnetic relaxation is expected in its MS spectrum.

3.2.MS data

3.2.1. MS data of the clinker

The MS spectra shown in Fig.3 of pure clinker, and impurities doped clinkers are similar. This means that the iron cations invironment wasn't affected by the addition of impurity materials. This result confirm that all the used impurities in clinker have the tendency to react with calcium silicate phases rather than with calcium aluminate phases; specially with the iron bearing phase in clinker C_4AF. Fig. 3a. shows that the spectrum of clinker prepared from pure oxides, is different from that of previously prepared clinker made from natural raw materials /8/. This spectrum was analysed into two doublets representing Fe^{3+} ions in both tetrahedral and octahedral sites. Where generally Fe^{2+} cations were not present in pure clinker /8/.

3.2.2. MS data of the ferrite phase

As in our previous study /4/ we can observe a paramagnetic doublets in case of pure C_4AF, see Fig. 4a. This spectrum was affected by adding the impurities into the raw mix of the ferrite phase which shows a superparamagnetic relaxation. This transformation may be due to the role of impurities in making very small particle size as the sample was quenched in air. This relaxation was observed previously when the C_4AF composition was not stoichiometric /9, 10/. Generally, the magnetic microcrystals with dimensions of the order of 100 Å often exhibit superparamagnetic relaxation with a relaxation time in range 10^{-7}-10^{-11} s /11/.

The ferrite with CaF_2, ZnO, MgF_2 or $CaCl_2$ shows one doublet with isomer shift of 0.4 mm/s and quadrupole splitting of 1.7 mm/s. The ferrite with LiF and the pure ferrite exhibited two doublets, similar to the ferrite doped with alkali oxides /4/. The two doublets have isomer shift 0.33, 0.84 mm/s, and quadrupole splitting 1.33, 1.98 mm/s respectively of Fe^{3+} cations in the octahedral and tetrahedral sites.

The temperature below which small magnetic particles behaves like a magnetically ordered crystal is known as the blocking temperature T_B/11/. Where for Fe-57 MS T_B may be defined as the temperature at which the relaxation time is of the order 2.5×10^{-9}s /12/. The blocking temperature of each ferrite was determined from Mössbauer spectra by increasing the temperature see Fig. 4. The blocking temperature was found to be 460 °K for ferrites doped with LiF or CaF_2, 380 °K for ferrites doped with MgF_2 or ZnO and 420 °K in case of $CaCl_2$ doping.

4. CONCLUSIONS

The differences between the MS spectra of the pure clinker and pure ferrite phase which is made of four major phases with the clinker, confirming that the clinker is a solid solution and not a mixture of these phases. While impurity doping led to the formation of small size particles. The LiF doping gave the smallest particle size and consequently the highest blocking temperature. The ferrite with LiF exhibited two Fe^{3+} sites, while the other impurities showed only one site. The superparamagnetic relaxation appeared only in spectra of ferrite doped impurities, which means that the impurities in clinker have a tendency to combine with the calcium silicate phases.

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