

Study of the Hydration of Blast-Furnace Slag Cement and Portland Cement by Mossbauer Spectroscopy

by

N. A. Eissa, M. Y. Hassaan, S. H. Salah,
Physics Department, Faculty of Science, Al-Azhar University
Nasr City, Cairo, Egypt.

and

H. A. Sallam, S. A. Abo-El-Enein
Faculty of Science, Qatar University,
Doha, Qatar.

ABSTRACT

Mossbauer spectra have been measured for the hydrated blast-furnace slag cement and Portland cement pastes at different times of hydration of 1, 3, 7, 28 and 90 days. The spectra showed the existence of iron atoms, $\text{Fe}^{3+}(\text{T})$ and $\text{Fe}^{3+}(\text{O})$ states of iron. It was found that, as the time of hydration was increased, the $\text{Fe}^{3+}(\text{O})$ content decreased, while the $\text{Fe}^{3+}(\text{T})$ content increased. The $\text{Fe}^{3+}(\text{T}) / \sum \text{Fe}^{3+}$ percentage was calculated for the two types of cement as a function of the time of hydration. A correlation has been found between this ratio and the compressive strength of the hardened cement paste.

Introduction

Recently, the Mossbauer effect (ME) technique has been applied in the cement industry⁽¹⁻⁶⁾. Wittmann et al⁽¹⁾ proposed that the degree of hydration of cement could be determined from the change in ME spectra with hydration time. In the present work this proposal has been realized and extended to a correlation between the degree of hydration as calculated from the ME spectra and the compressive strength of the hardened cement paste.

Experimental

Two kinds of dry cements having a Blaine area of 3000 cm²/g were used, these are the blast-furnace slag cement, having a slag content of 35:65 by weight of portland cement, and Portland cement, both cements were supplied by the National Cement Company, Tabbin, Helwan, Cairo, Egypt. The pastes were made by mixing each cement with water, using a water/cement ratio of 0.40 (by weight). After attaining the final setting of the paste within the cubic inch moulds, the pastes were demoulded and then cured under water at room temperature until the desired time of testing was reached. The hydration time intervals were 1, 3, 7, 28 and 90 days.

Compressive strength tests were carried out at each age of hydration by using the cubic cement pastes; the crushed samples were then ground to pass completely through a 170 mesh sieve. A sample of 200 mg of the ground hydrated cement was pressed into a disc form to be used as a ME absorber.

The ME spectra were measured using a conventional constant acceleration electromechanical drive coupled to a 512 multichannel analyser. The velocity scale was calibrated using metallic iron foil and the source used was about 30 millicurie radioactive⁵⁷ Co diffused in a cubic non-magnetic chromium lattice. All spectra were measured at room temperature.

Results and Discussion

The ME spectra of the cement constituents are shown in Fig. (1). The blast-furnace slag showed an unestimatable quantity of metallic iron while the industrial clinker spectrum showed the iron in the ferrous state Fe²⁺, the ferric ions in the tetrahedral state Fe³⁺(T) and the ferric ions in the octahedral state Fe³⁺(O). Fig. (2) shows the ME spectra of the blastfurnace slag cement pastes hydrated for different times. The Portland cement pastes hydrated for the same different times shows spectra similar to that spectra of blast-furnace slag cement pastes.

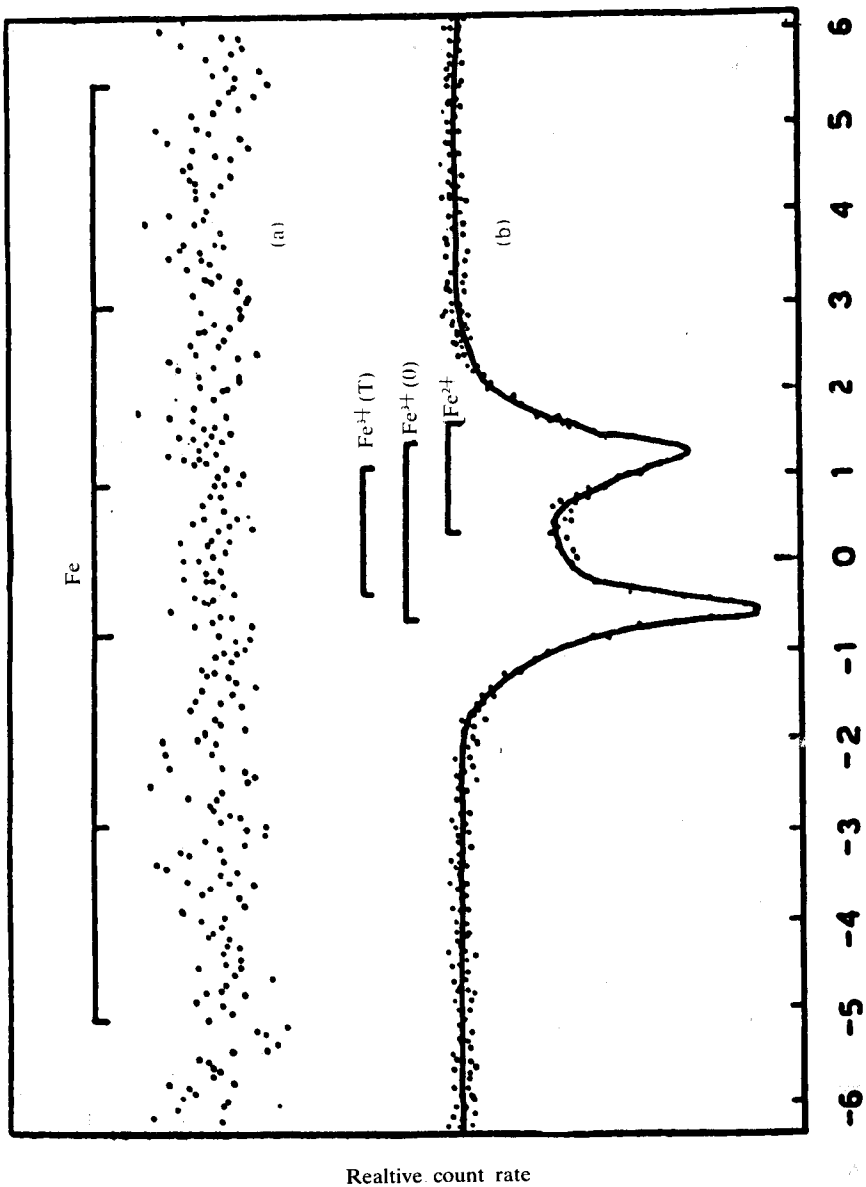


Fig. 1: Mössbauer spectra of: (a) blastfurnace slag (b) Industrial clinker

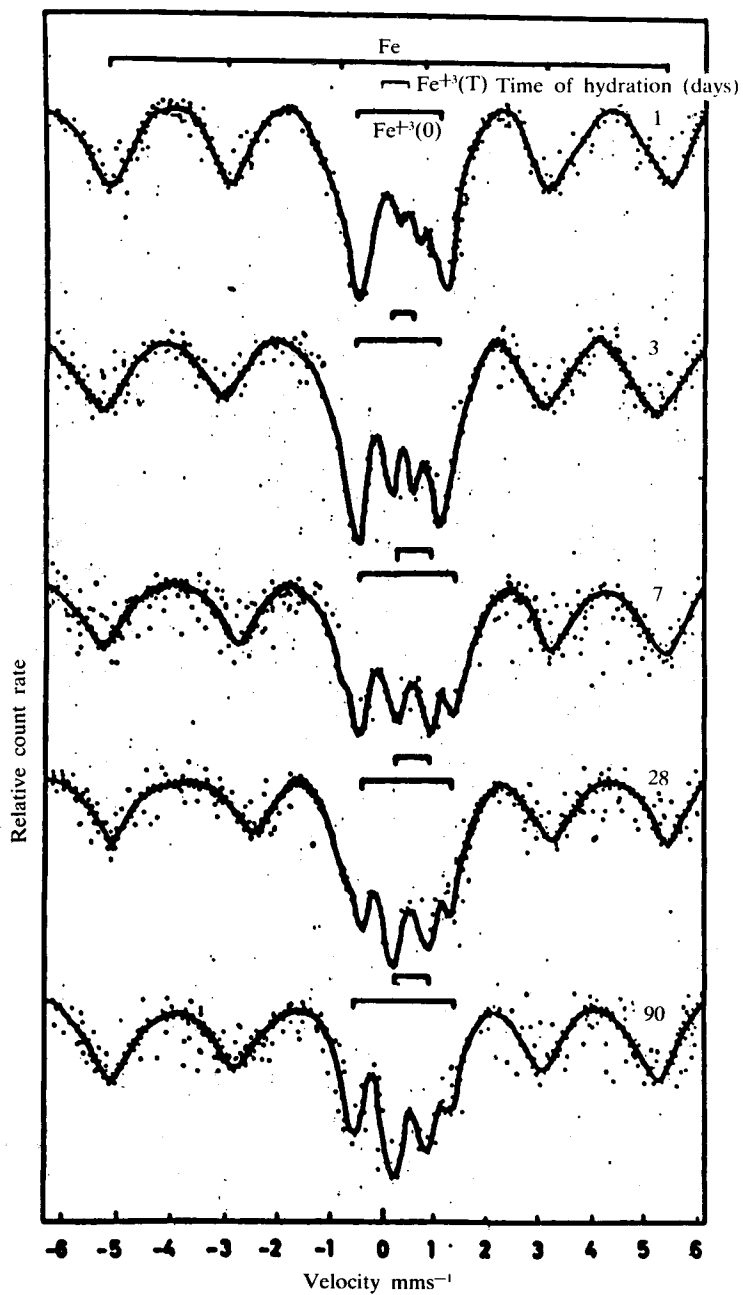


Fig. 2: Mossbauer spectra of the hydrated blastfurnace slag cement paste.

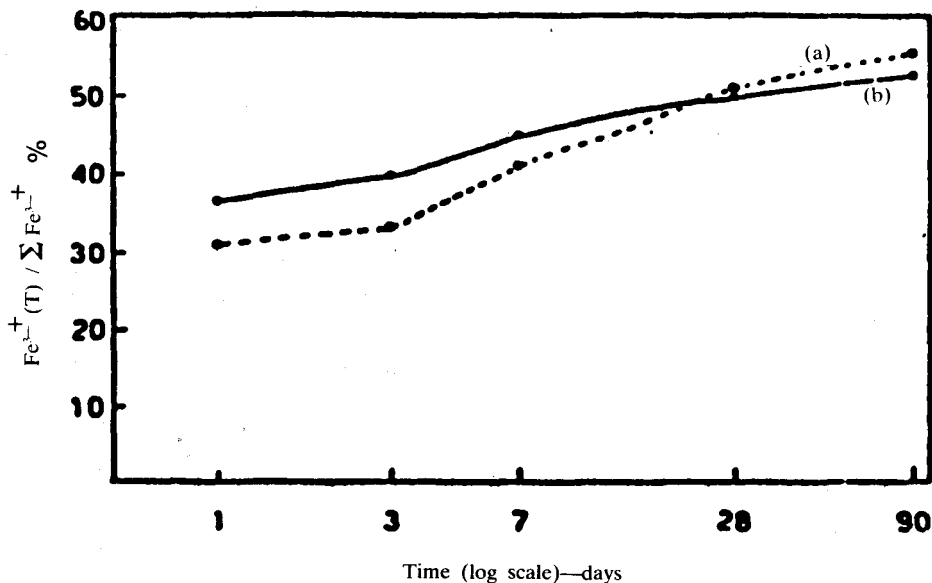


Fig. 3: Hydration of: (a) blastfurnace slag cement paste and (b) Portland cement paste.

The analysis of these spectra showed that the amount of $Fe^{3+}(T)$ was increased with increasing the time of hydration, while the amount of the $Fe^{3+}(0)$ was decreased. After one day of hydration the six lines of the iron atoms appeared in the ME spectra and the Fe^{2+} state disappeared, this may be due to the reaction $3 Fe^{2+} \rightarrow 2 Fe^{3+} + Fe$. The percentage of the iron atoms remained constant at the different times of hydration. The ME parameters for the two ferric states in the hydrated blastfurnace slag cement and the hydrated Portland cement were found to be constant with increasing the time of hydration. Fig. (3) shows the compressive strength values as calculated from $Fe^{3+}(T) / \sum Fe^{3+}$ percentage for different times of hydration. The obtained curves indicated higher values of $Fe^{3+}(T) / \sum Fe^{3+}$ percentage (expression for the degree of hydration) in the hydrated Portland cement greater than those obtained for the hydrated blast furnace slag cement during the early stages of hydration, this results was reversed in the final stages of hydration.

The results shown in Fig. (4) represent a relation between compressive strength and the degree of hydration as calculated from the $Fe^{3+}(T) / \sum Fe^{3+} + \%$. The curves demonstrate higher strength values for the blast-furnace slag cement pastes

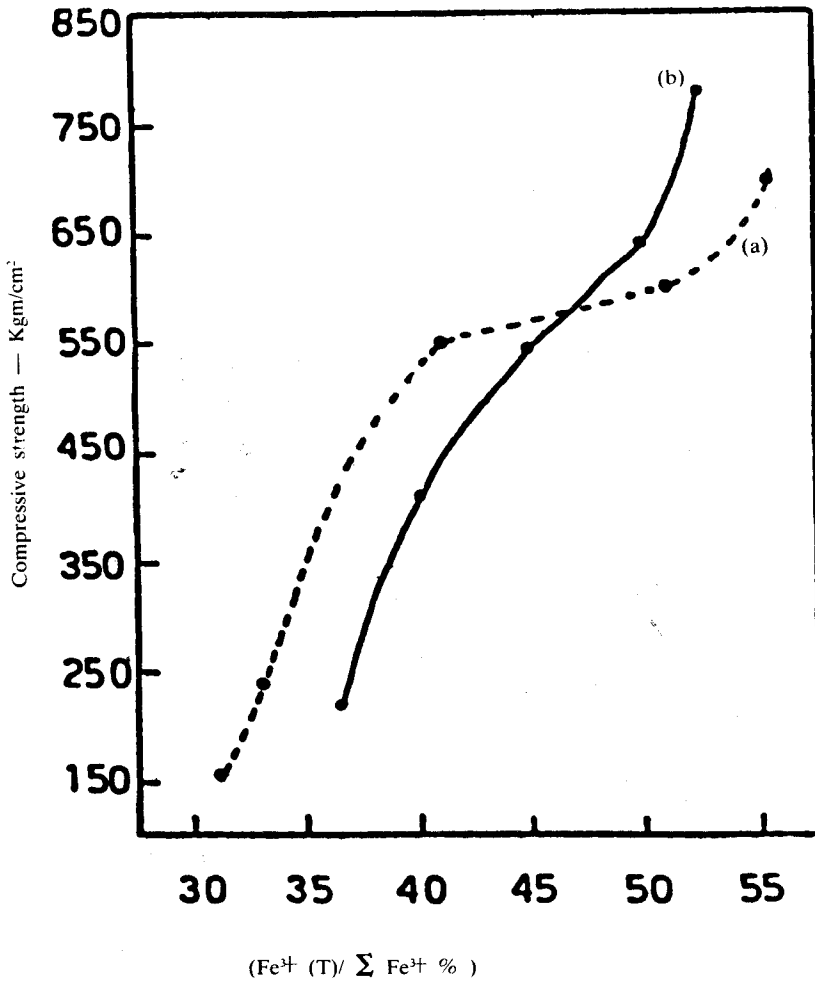


Fig. 4: Relation between $(Fe^{3+} (T) / \sum Fe^{3+} \%)$ and compressive strength of both hydrated (a) blastfurnace slag cement paste, (b) Portland cement paste.

during the early hydration stages when compared with the Portland cement pastes at the same values of degree of hydration. This result might be associated with the physical state of the hydration products themselves, namely, the ill-crystalline character of the hydrates obtained during the early stages of hydration of slag cement as compared with those obtained by the hydration of Portland cement. In the final stages of hydration, however, Portland cement pastes possess higher strength values than slag cement pastes when compared at the same value of degree of hydration.

Conclusion

The determination of the degree of hydration by the ME spectroscopy was demonstrated. A correlation between the degree of hydration or the compressive strength and the $\text{Fe}^{3+}(\text{T}) / \sum \text{Fe}^{3+} \%$ was established. The contribution of the hydration products to the strength development is different for slag cement than that for Portland cement, and the order is also different during the early stages of hydration than that in the final stages.

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دراسة عملية التأدرت لأسمنت خبث الأفران العالية والأسمنت الحديدي باستخدام ظاهرة موسباور

نبيل عيسى ، محمد يسري حسان ، صلاح هاشم صلاح

كلية العلوم - جامعة الأزهر

هناء سلام ، صلاح أبو العينين

كلية العلوم - جامعة قطر

ملخص

تم في هذا البحث دراسة أطياف موسباور لكل من عجائن أسمنت خبث الأفران العالية والأسمنت البورتلاندي بعد التأدرت لفترات زمنية مختلفة (يوم ، ثلاثة أيام ، سبعة أيام ، ثمانية وعشرون يوماً ، تسعون يوماً) ولقد أظهرت نتائج تحليل بارامترات موسباور لأطياف هذه العجائن أن هناك نقص في محتوى أيونات الحديد في المواقع ثمانية التأذر وزيادة أيونات الحديد في المواقع رباعية التأذر وذلك بزيادة زمن التأدرت .

وقد تم حساب النسبة المئوية لمحتوى أيونات الحديد رباعية الترابط إلى المحتوى الكلي لأيونات الحديد عند أزمنة التأدرت المختلفة لكل من نوعي الأسمنت تحت الدراسة ، وأمكن إيجاد علاقة بين قوة تحمل الضغط الميكانيكي للعجينة المتصلدة وقيم درجة التأدرت المحسوبة من هذه النسبة المئوية (ح⁺ / مجموع ح⁺) .