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**THE INCORPORATION OF Fe₂O₃, FeO
AND Al₂O₃ IN SILICATE GLASSES
AND ITS EFFECT ON THEIR STRUCTURE
AND CHEMICAL STABILITY**

P. VAN ISEGHEM, E. DE GRAVE, L. PETERS, R. DE BATIST



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Summary. - The structure and chemical stability of silicate glasses containing up to 30 mole % Fe₂O_x or (Fe₂O_x + Al₂O₃) (x = 2 or 3) were investigated. The main conclusions are :

- Both Fe³⁺ and Fe²⁺ ions occupy octahedrally and tetrahedrally coordinated sites in the glass matrix. The fraction tetrahedrally coordinated Fe²⁺ ions is probably larger than for Fe³⁺. It is suggested that the tetrahedral sites correspond to glass network forming sites.
- Up to 12.5 and 20 mole % Fe₂O₃ and Fe₂O₂, respectively, can be incorporated in the glass matrix.
- For Fe₂O_x smaller than 10 mole % the corrosion rates increase strongly with increasing Fe₂O_x (x = 2 or 3) content. No beneficial influence from the apparently larger amount tetrahedrally coordinated Fe²⁺ ions upon the corrosion rate is observed. Partial replacement of Fe₂O_x by Al₂O₃ yields decreased corrosion rates, especially for x = 3.
- For Fe₂O_x greater than 10 mole % the chemical stability of the Fe³⁺ glasses is a factor x 10 better than for the corresponding Fe²⁺ glasses (both with and without Al₂O₃), due to the beneficial effect of a magnetite (Fe₃O₄)-like spinel phase which is formed upon glass preparation.

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Samenvatting. - De structuur en de chemische stabiliteit van silikaatglazen die tot 30 mol. % Fe₂O_x of (Fe₂O_x + Al₂O₃) (x = 2 of 3) bevatten, werden onderzocht. De voornaamste besluiten zijn :

- Zowel Fe³⁺ als Fe²⁺ ionen bezetten oktaëdrisch en tetraëdrisch gekoördineerde posities in de glasmatrix. De fractie der tetraëdrisch gekoördineerde Fe²⁺ ionen is waarschijnlijk groter dan voor de Fe³⁺ ionen. Er wordt gesuggereerd dat de tetraëdrische posities overeenstemmen met glasnetwerkvormende posities.
- Tot 12,5 en 20 mol. % respectievelijk Fe₂O₃ en Fe₂O₂ kunnen worden ingebouwd in de glasmatrix.
- Voor Fe₂O_x kleiner dan 10 mol. %, nemen de korrosiesnelheden aanzienlijk toe met toenemend Fe₂O_x (x = 2 of 3) gehalte. Een gunstige invloed van de blijkbaar grotere hoeveelheid tetraëdrisch gekoördineerde Fe²⁺ ionen op de korrosiesnelheid wordt niet waargenomen. De gedeeltelijke vervanging van Fe₂O_x door Al₂O₃ resulteert in lagere korrosiesnelheden, in het bijzonder voor x = 3.
- Voor Fe₂O_x groter dan 10 mol. %, is de chemische stabiliteit van de Fe³⁺ glazen een factor x 10 beter dan voor de overeenstemmende Fe²⁺ glazen (zowel met als zonder Al₂O₃), dank zij de gunstige invloed van een magnetietachtige (Fe₃O₄) spinelfaze die zich tijdens de glasbereiding zelf vormde.

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Résumé. - La structure et la stabilité chimique de verres silicatés contenant jusqu'à 30 mol. % Fe₂O_x ou (Fe₂O_x + Al₂O₃) (x = 2 ou 3) ont été examinées. Les conclusions principales sont les suivantes.

- Tant les ions Fe³⁺ que Fe²⁺ occupent des positions coordonnées de façon octaédrique et tétraédrique dans la matrice du verre. La fraction des ions Fe²⁺ avec une coordonnance tétraédrique est probablement plus grande que celle des ions Fe³⁺. Nous suggérons que les positions tétraédriques correspondent à des positions formateur de réseau du verre.
- Jusqu'à 12,5 et 20 mol. % respectivement de Fe₂O₃ et Fe₂O₂ peuvent être incorporés dans la matrice de verre.
- Pour Fe₂O_x inférieur à 10 mol. %, les vitesses de corrosion augmentent sensiblement avec la teneur Fe₂O_x (x = 2 ou 3). Une influence positive de la quantité apparemment plus élevée d'ions Fe²⁺ avec coordonnance tétraédrique n'a pas été observée. Le remplacement partiel de Fe₂O_x par Al₂O₃ résulte en des vitesses de corrosion plus basses, plus particulièrement pour x = 3.
- Pour Fe₂O_x supérieur à 10 mol. %, la stabilité chimique des verres Fe³⁺ est meilleure d'un facteur x 10 que pour les verres Fe²⁺ correspondants (tant avec que sans Al₂O₃), grâce à l'effet bénéfique d'une phase «spinel» magnétite (Fe₃O₄) formée. Cette phase se forme lors de la préparation des verres.

THE INCORPORATION OF Fe_2O_3 , FeO AND Al_2O_3 IN SILICATE GLASSES AND ITS
EFFECT ON THEIR STRUCTURE AND CHEMICAL STABILITY

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INTRODUCTION

Large amounts of the glass intermediates Al_2O_3 , Fe_2O_3 and FeO are present in the amorphous silicate slags developed at the S.C.K./C.E.N. for the conditioning of Pu contaminated radioactive waste. Strong ambiguity exists in literature about both the structural incorporation and the effect on the chemical stability of Fe_2O_3 and FeO . The chemical stability and its relationship to the glass structure therefore was investigated for a number of silicate base glasses, taking into consideration the following parameters (the amount of glass modifiers was kept constant at 16 mole %, equimolarly spread over Li_2O , K_2O , MgO and CaO):

- 1) Fe_2O_x concentrations ($x = 2$ or 3) varying between 2.5 and 30 mole % (compensated by changes in SiO_2 concentration);
- 2) Equimolar replacement of Fe_2O_x by Al_2O_3 and Fe_2O_x in all glasses listed in 1. The structural incorporation of Fe_2O_x was investigated by ^{57}Fe Mössbauer Spectroscopy, the chemical stability by the Soxhlet corrosion test. The sample weight was measured after 14 days of corrosion, after drying and removal of the weakly bounded surface layer.

RESULTS FROM MOSSBAUER ANALYSES (Figs 1-3)

Fe^{3+} GLASSES (prepared under ambient atmosphere)

$\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ranges between 0.7 and 0.8.

Two doublets are resolved for Fe^{3+} , with respective quadrupole splitting (ΔE_Q) values of 0.75 - 0.85 and 1.25 - 1.40 mm/s. Isomer shift (IS) values* are between 0.10 and 0.20 mm/s for both doublets.

Resolution of two doublets for Fe^{2+} is also possible, but less significant due to the low Fe^{2+} content. The ΔE_Q values are 1.65 - 1.75 and 2.0 - 2.10 mm/s, respectively.

Up to 12.5 mole % Fe_2O_3 or $(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ can be incorporated in the silicate glass matrix. Above 12.5 mole % a magnetic Fe_3O_4 -like spinel phase is precipitated.

Fe^{2+} GLASSES (prepared under Argon atmosphere)

$\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ranges between 0.7 and 0.9.

Careful interpretation of the Fe^{3+} spectrum is difficult due to the small Fe^{3+} content. The spectra were fitted with one Fe^{3+} doublet, with $\Delta E_Q \approx 0.50$ mm/s, IS between 0.5 and 0.6 mm/s and a line width (Γ) 0.70 - 0.85 mm/s.

The Fe^{2+} absorption was fitted with five doublets. The weighed averages for ΔE_{Q_i} vary between 1.8 and 2.0 mm/s. The smaller ΔE_{Q_i} in the distribution correspond to the smaller IS_i , the larger ΔE_{Q_i} to the larger IS_i , but a simple and unique relation between these Mössbauer parameters could not be observed.

Up to 20 mole % Fe_2O_2 and up to 30 mole % $(\text{Fe}_2\text{O}_2 + \text{Al}_2\text{O}_3)$ can be incorporated in the silicate glass matrix.

Partial replacement of Fe_2O_3 or Fe_2O_2 by Al_2O_3 does not influence the Mössbauer spectra.

*All IS-values are quoted against metallic Fe at ambient temperature.

RESULTS FROM SOXHLET CORROSION TESTS (Fig. 4)

 Fe^{3+} GLASSES

The corrosion rates increase steeply between 2.5 and 10 mole % Fe_2O_3 , and decrease for % Fe_2O_3 between 15 and 30 mole %.

Partial replacement by Al_2O_3 results in a fairly constant, low corrosion rate between 5 and 20 mole % ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$).

 Fe^{2+} GLASSES

The corrosion rates increase steeply with increasing Fe_2O_2 content up to 10 mole %, whereafter the corrosion rate roughly remains constant.

Partial replacement by Al_2O_3 results in slower increasing corrosion rates with increasing ($\text{Fe}_2\text{O}_2 + \text{Al}_2\text{O}_3$) content, reaching the same values as for the non Al_2O_3 glasses for 20 mole % ($\text{Fe}_2\text{O}_2 + \text{Al}_2\text{O}_3$).

Both Fe^{3+} and Fe^{2+} glasses exhibit weakly bounded surface layers upon corrosion, whose thickness increases with increasing corrosion rate (e.g. 0.05 and 10 μm for Fe^{2+} glasses with 2.5 and 17.5 mole % Fe_2O_2 , without Al_2O_3). These surface layers result from dealcalization and subsequent hydration, not by precipitation from the leachate, and are essentially Fe enriched. No weakly bounded surface layers were formed in case of the partly crystalline Fe^{3+} and Fe^{2+} glasses.

DISCUSSION

Fe^{3+} appears to be mainly octahedrally coordinated in both Fe^{3+} and Fe^{2+} glasses. A small part of Fe^{3+} is tetrahedrally coordinated in the Fe^{3+} glasses. Fe^{2+} seems to occur both in tetrahedral and octahedral coordination states in comparable amounts, in both Fe^{3+} and Fe^{2+} glasses. A quantitative distribution between tetrahedrally and octahedrally coordinated Fe^{2+} ions is difficult to calculate, due to its weak occurrence (Fe^{3+} glasses) or the large variety of Fe^{2+} incorporation modes (Fe^{2+} glasses). No evidence for an influence of Al_2O_3 on the distribution of the Fe^{2+} and Fe^{3+} coordination states has been found. We suggest that tetrahedrally coordinated Fe^{3+} and Fe^{2+} occupy network forming positions. This implies the addition of one or two, respectively, compensating charges (Li^+ , K^+ , Ca^{2+} , Mg^{2+}) to the FeO_4 tetrahedra. Fe^{2+}O_4 tetrahedra therefore subtract more network modifiers from the interstitial sites than Fe^{3+}O_4 tetrahedra do, which is confirmed by the larger amount of Fe_2O_2 which can be incorporated in the glass matrix.

The increase of the corrosion rate for increasing Fe_2O_x content up to 10 mole % relates to the increase in network modifier (Fe^{3+} , Fe^{2+}) content. Partial substitution by Al_2O_3 reduces this corrosion rate increase. The Fe^{2+} glasses, both with and without Al_2O_3 , although yielding a larger amount of tetrahedrally coordinated Fe ions than the Fe^{3+} glasses do not exhibit a better corrosion resistance. For Fe_2O_x or $(\text{Fe}_2\text{O}_x + \text{Al}_2\text{O}_3) > 10$ mole %, the much smaller corrosion rates for the Fe^{3+} glasses relative to the Fe^{2+} glasses is due to the precipitation of magnetite-like crystals, which reinforces the residual glass matrix.

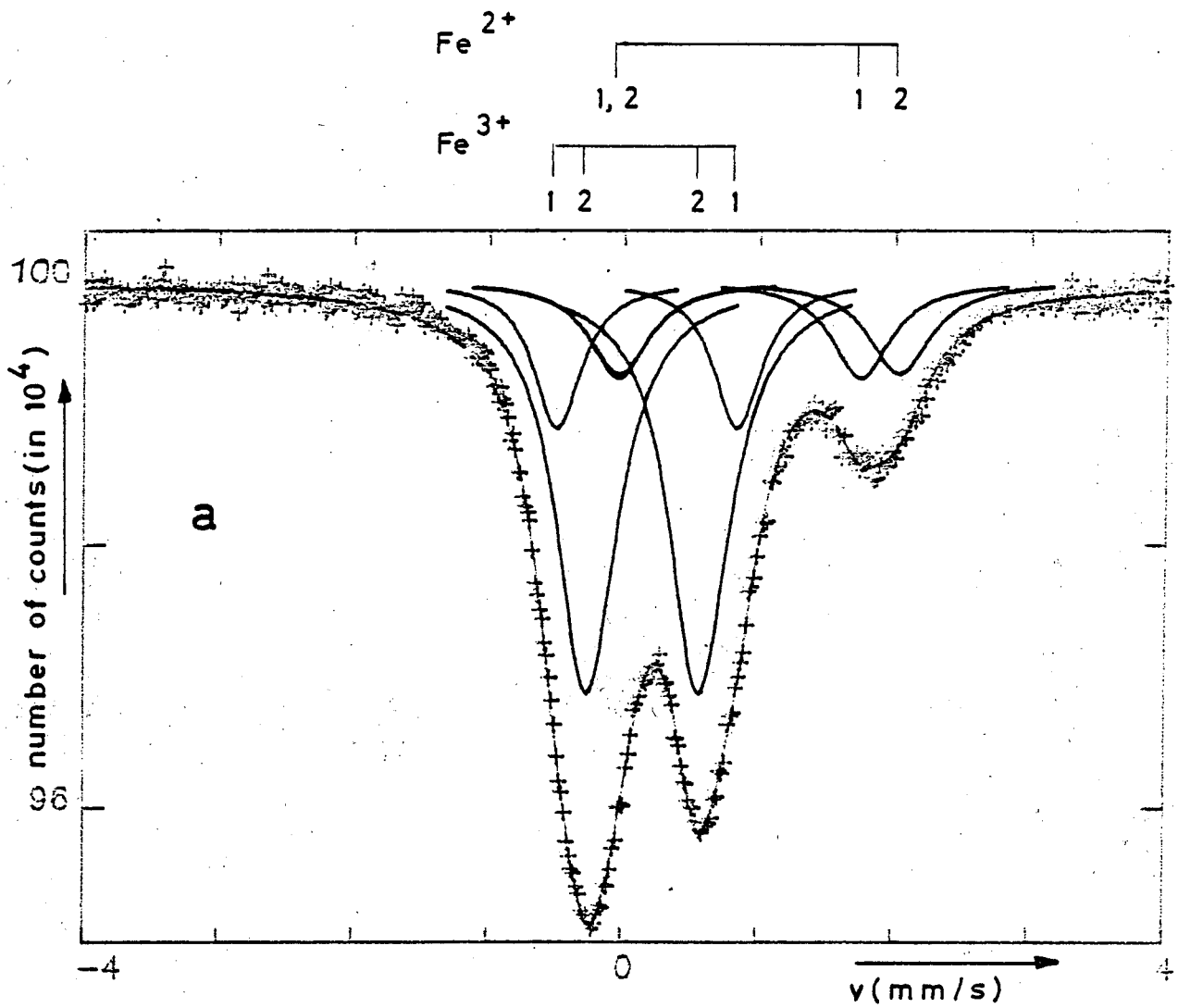


FIG.1 : MOSSBAUER SPECTRUM FOR THE Fe^{3+} GLASS CONTAINING 7.5 MOLE % Fe_2O_3

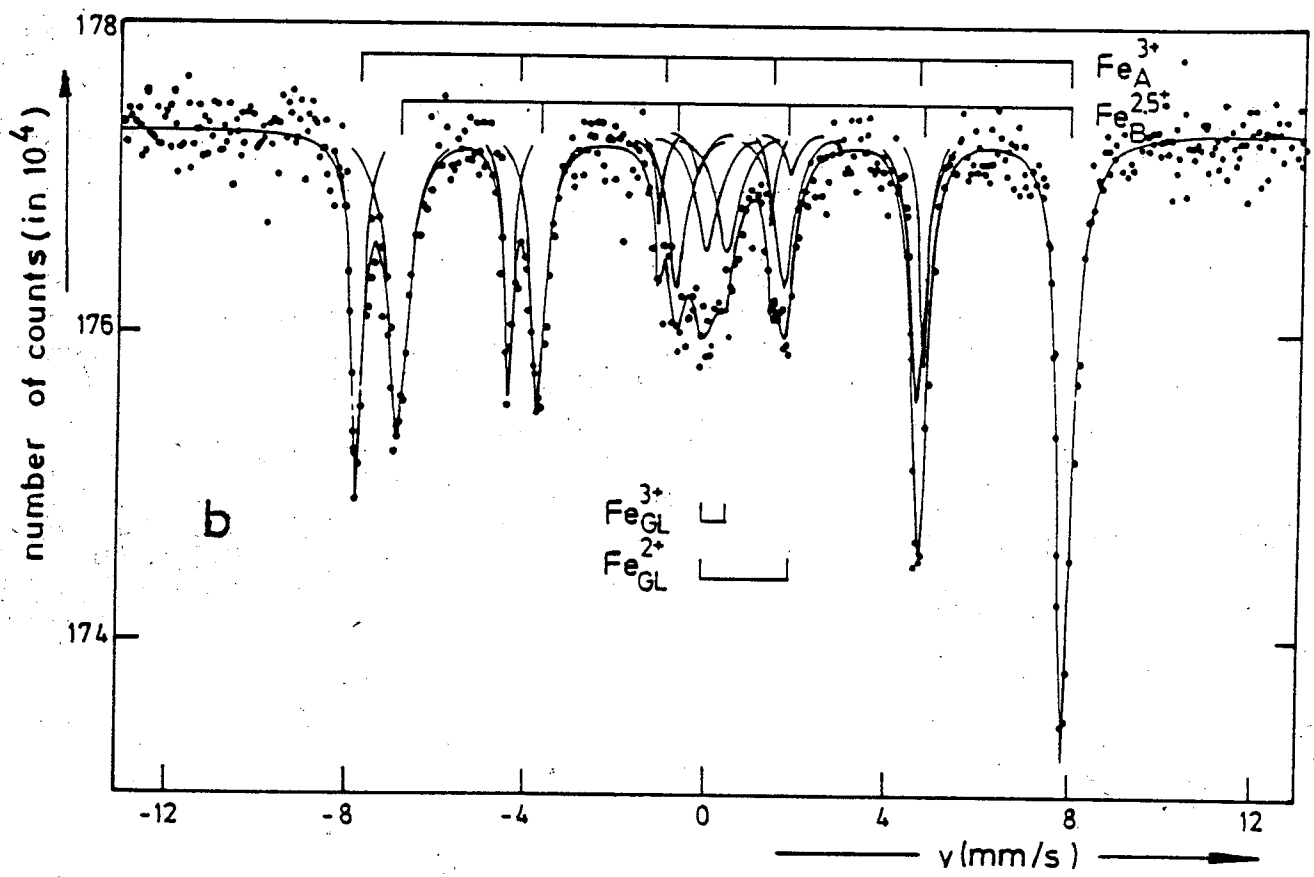


FIG.2 : MOSSBAUER SPECTRUM FOR THE Fe³⁺ GLASS CONTAINING 30 MOLE % Fe₂O₃

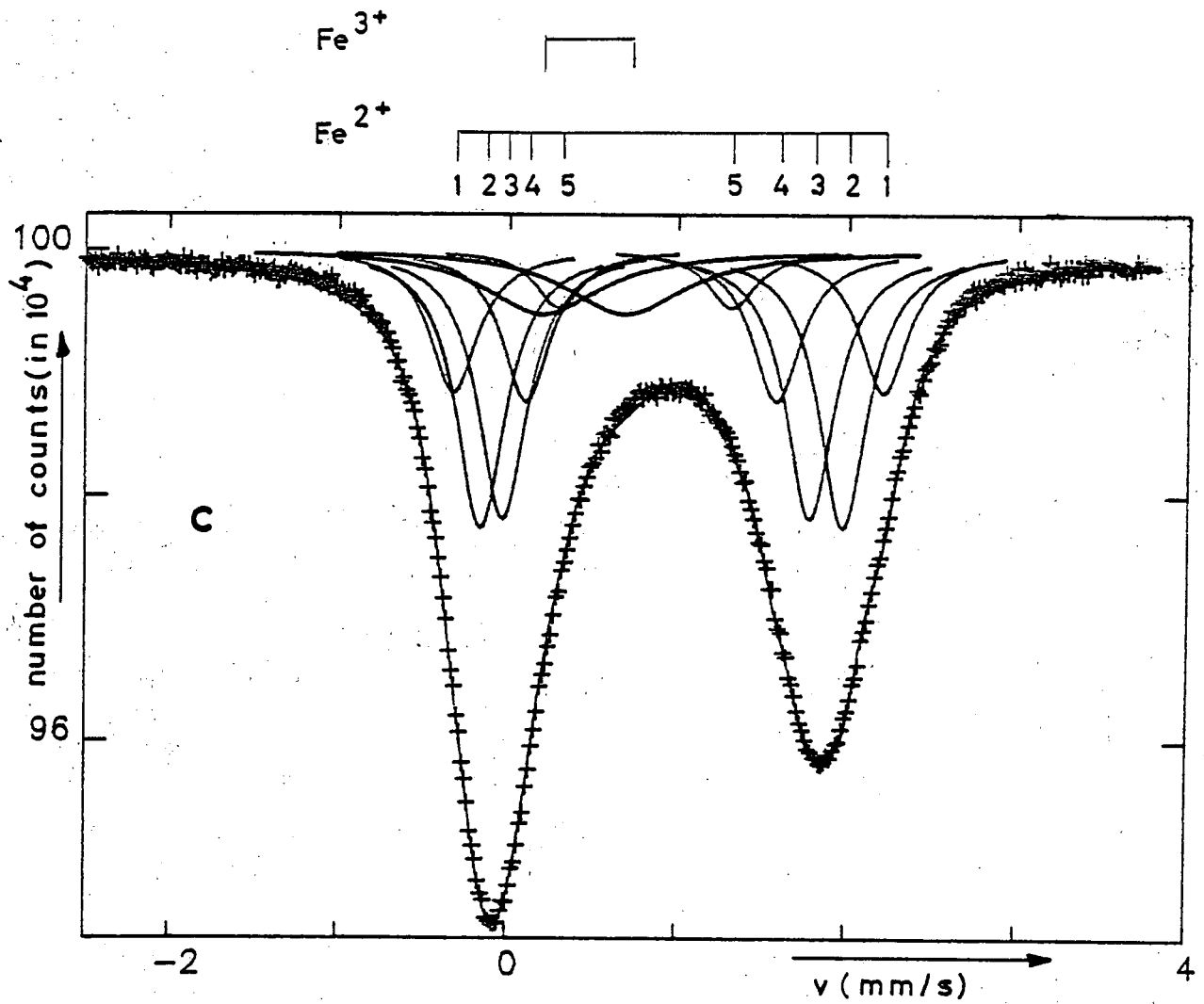


FIG.3 : MOSSBAUER SPECTRUM FOR THE Fe^{2+} GLASS CONTAINING 7.5 MOLE % Fe_2O_3

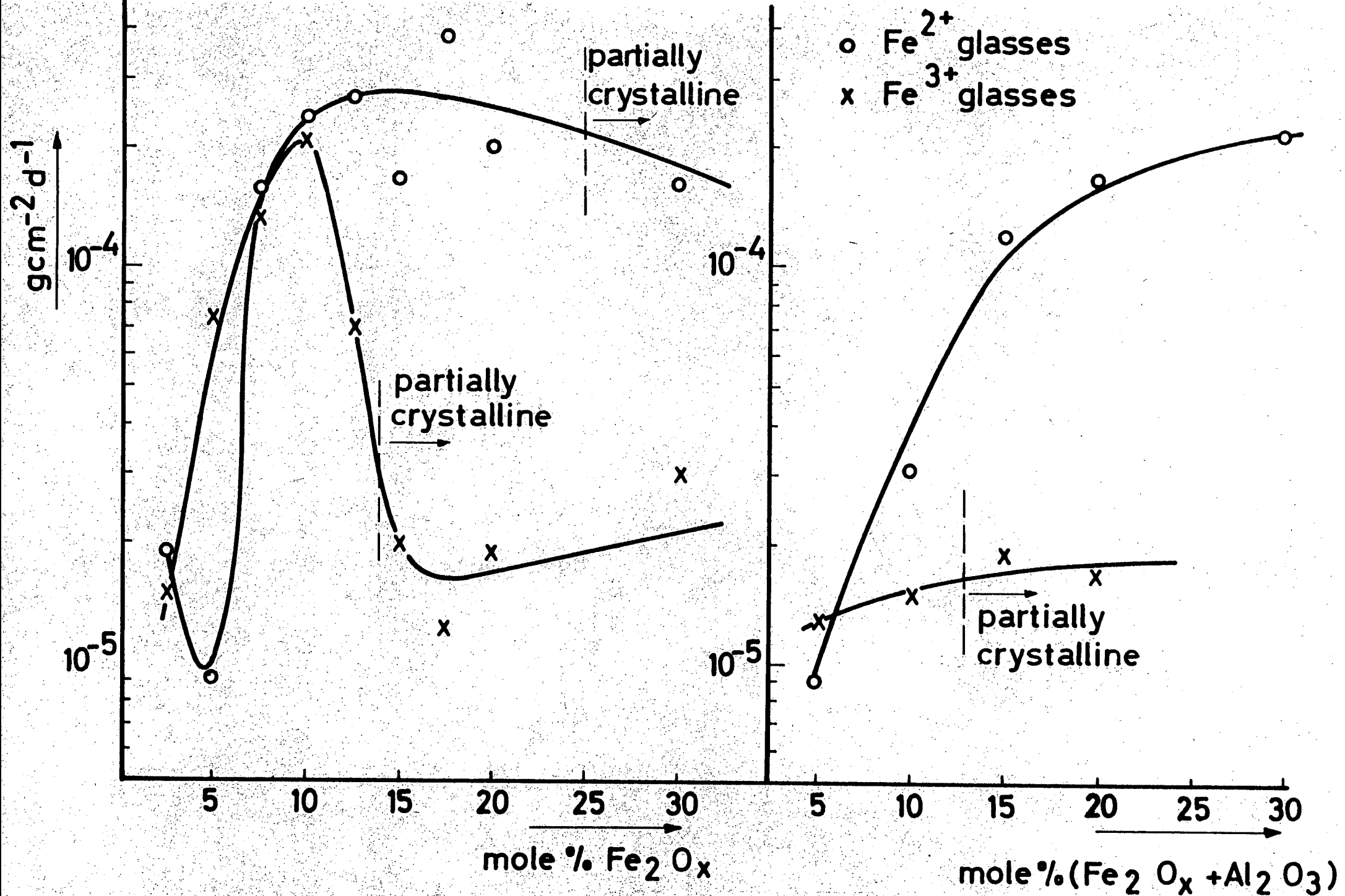


FIG.4 : SOXHLET CORROSION RATES AS A FUNCTION OF THE Fe_2O_x OR $(\text{Fe}_2\text{O}_x + \text{Al}_2\text{O}_3)$ CONTENT ($x = 2$ OR 3).

