

MÖSSBAUER STUDY OF THE ATTENUATION OF IRON IN AN IRRIGATED GREENSAND LYSIMETER

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Abstract— Fe^{57} Mössbauer spectroscopy has been used to determine the nature of iron-containing minerals in Lower Greensand samples from an experimental lysimeter at Uffington, Oxfordshire, both before and after a three-year irrigation with a synthetic heavy metal leachate. Analysis of the spectra measured at 300°, 77°, and 4.2°K and at 4.2°K in an applied field of 45 kOe shows that iron is present in the uncontaminated sandstone in fine-grained goethite (α - $FeOOH$) and glauconite. In the irrigated samples iron is precipitated as a fine-grained ferric hydroxide gel having values for the hyperfine field at 4.2°K of 435 and 470 kOe. The stability of the gel over the three-year period of irrigation may be explained by surface energy considerations.

Key Words—Glauconite, Goethite, Greensand, Iron, Lysimeter, Mössbauer spectroscopy.

INTRODUCTION

Although the processes controlling the migration of pollutant ions are complex (see, e.g., Langmuir, 1972), heavy metals may be strongly attenuated by hydrous oxides of iron and manganese which provide a matrix for the sorption, coprecipitation and occlusion in sediments (Jenne, 1968, 1976). Kinniburgh (1974) reported that the degree of crystalline order in such oxides affects both the total sorptive capacity for hydrolyzable metal ions and their specific adsorption. An increase in the degree of crystallinity leads to a decrease in the number of adsorption sites, but to an increase in the number of highly selective sites. He proposed that these phenomena result from steric and size constraints, which limit solid state diffusion into the adsorbent material. Because certain ions, such as Cd^{2+} and Pb^{2+} , do not undergo substitution for Fe^{3+} in crystal lattices and are retained principally by surface adsorption on iron oxides, their long-term retention may be limited by the nature of the iron oxide phase in the sediment and by any phase changes occurring subsequently.

The aim of the present study was to determine the nature of iron-bearing phases in sediment samples from an experimental lysimeter, before and after a three-year irrigation with a synthetic, heavy-metal leachate solution. Mössbauer spectroscopy was used to identify the iron-bearing minerals because diagnostic spectra for iron oxides can be obtained for particles much smaller than those required for routine X-ray powder diffraction analysis ($\sim 1000 \text{ \AA}$). However, these spectra may be quite different from those expected for the oxides in

bulk form due to relaxation effects, and spectra at several temperatures were therefore necessary, allowing the contribution from iron in the clay minerals to be resolved. The differentiation of finely divided ferromagnetic oxides, such as magnetite and maghemite, from antiferromagnetic oxides, such as hematite and goethite, was made by comparing the spectra obtained at 4.2°K in a zero field with those obtained in a large magnetic field ($\geq 10 \text{ kOe}$) (Longworth and Tite, 1977). The distinction was made on the basis of changes both in the hyperfine splitting and in the relative intensity of lines 2 and 5 in the spectrum.

EXPERIMENTAL

Samples

Samples were obtained from an experimental lysimeter which had been designed to study heavy metal-sediment interactions under controlled conditions analogous to those in the unsaturated zone beneath landfill disposal sites (Black *et al.*, 1976). The lysimeter, constructed in the Lower Greensand at a site near Uffington, Oxfordshire, was irrigated for nearly four years with a synthetic leachate solution (Table 1) having a composition similar to that of a leachate which might result from the co-disposal of domestic wastes with industrial materials, such as metal-finishing sludges.

The Lower Greensand is a well-bedded sequence of poorly cemented fine sands and sandy clays of Cretaceous age, with quartz as the dominant mineral and as much as 20% calcium montmorillonite. Detrital glauconite and calcite are present in intermediate amounts, together with traces of aragonite, pyrite, and poorly

Table 1. Synthetic leachate composition.

Constituent	Concentration (mg/liter)	Constituent	Concentration (mg/liter)
Cadmium	100	Nickel	100
Calcium	500	Potassium	900
Chromium (III)	100	Sodium	1000
Copper	100	Zinc	100
Iron (II)	100	Chloride	1600
Lead	100	Acetic Acid	5000
Magnesium	100	Propionic Acid	3000
Mercury	10	Butyric Acid	2000
Lithium	20	Phenol	20

crystalline iron oxides: Core samples used in the Mössbauer study were collected before, and 300 and 750 days after the start of irrigation. After air-drying, the samples were disaggregated and mixed to provide a representative sample of the upper 40 mm of the lysimeter where heavy metal concentrations were found to be greatest (Ross, 1978). A further sample (750-day irrigation) treated to remove all but the "moderately reducible" and the residual silicate material was also examined by Mössbauer spectroscopy.

The distribution of heavy metals in selected fractions of lysimeter sediment samples, after 750 days irrigation, is listed in Table 2. Chemical phase analysis was performed using a sequential selective extraction scheme based upon that of Gupta and Chen (1975).

Instrumental techniques

Mössbauer spectra were measured using a 50 mCi Co^{57} -in-rhodium source and a constant acceleration Mössbauer spectrometer. The absorbers were prepared by mixing 200–300 mg of sample in vacuum grease and mounting the paste in a lead collimator. The spectra were measured at room temperature (Figure 1), 77°K, and 4.2°K (Figures 2 and 3) using conventional cryostats, and at 4.2°K in a magnetic field of 45 kOe (Figure 4), parallel to the direction of the γ -ray beam, using a superconducting solenoid. Spectra were also

Table 2. Distribution of heavy metals in selected chemical fractions as a percentage of each element extracted.

Fraction	Pb	Cu	Zn	Ni	Cd	Fe
A	27	19.6	17.3	14.7	11.6	21.4
B	—	2.7	9.8	5.6	2.7	35
C						43.4

A = Easily reducible oxide; soluble in 0.1 M hydroxylamine hydrochloride in 0.01 M nitric acid. (Iron concentration includes additional 6% nitric acid extraction.)

B = Moderately reducible oxide; 2% (w/w) sodium dithionite in 8% (w/w) sodium citrate solution.

C = Residual silicate fraction; 6 ml nitric acid + 4 ml hydrofluoric acid + 3 ml perchloric acid.

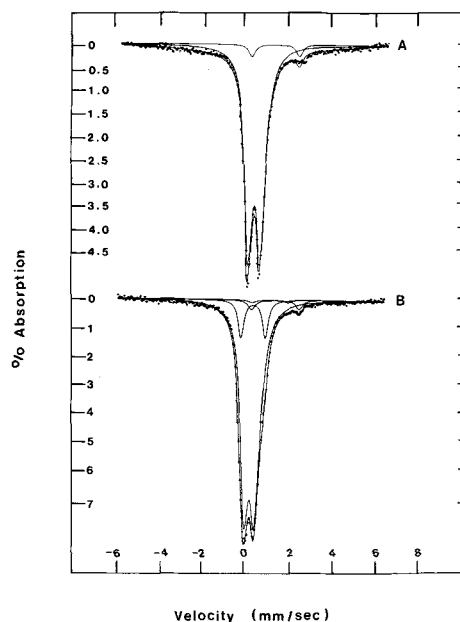


Figure 1. Fe^{57} Mössbauer spectra at room temperature for A, original Lower Greensand and B, glauconite. The solid lines indicate the total and component fits to the data as determined in the least squares minimization program. The zero of the velocity scale refers to the shift of α -iron.

measured for a sample of pelletal glauconite (Figures 1 and 4) of similar composition to that present in the Lower Greensand.

The spectra in zero applied field were fitted to a superposition of Lorentzian lines, using a least squares minimization program. The lines in the applied field spectra are very broad (~ 2 mm/sec) arising from a distribution of internal fields (H). Since it is difficult to predict the shape of this distribution it was determined

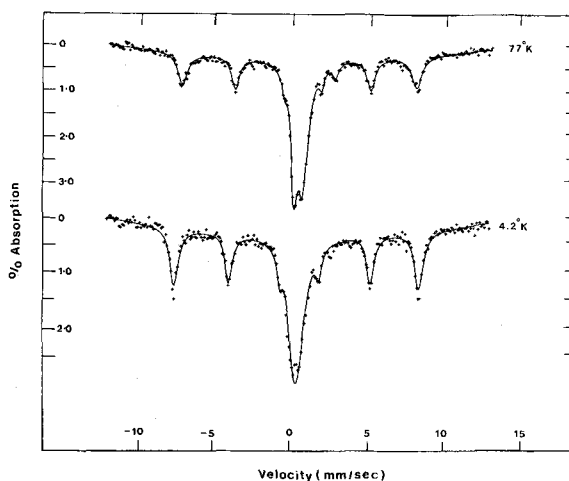


Figure 2. Fe^{57} Mössbauer spectra at 77°K and at 4.2°K for original Lower Greensand.

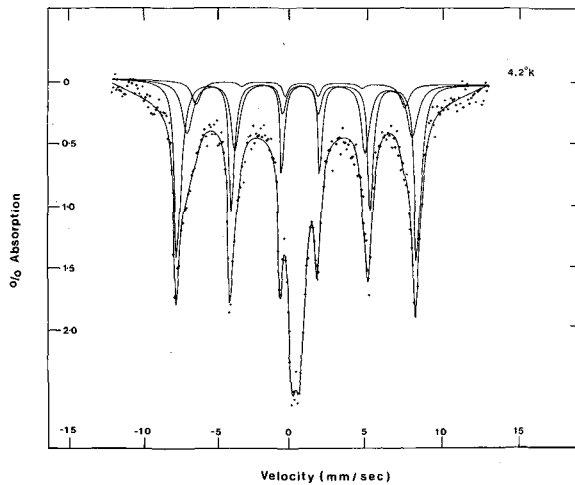


Figure 3. Fe^{57} Mössbauer spectra at 4.2°K for Lower Greensand irrigated for 750 days.

empirically using a series expansion. Specifically, the probability distribution of field $P(H)$ is approximated by a set of trigonometrical functions whose coefficients are determined by least squares analysis (Window, 1971). This method is more effective for broad distributions, such as those occurring in the applied field spectra (Figures 4 and 5). For narrow distributions a greater number of functions is required, and, if the quality of the spectrum is relatively poor, spurious field values corresponding to statistical fluctuations in the data may be obtained.

The hyperfine parameters are listed in Tables 3, 4, and 5. The total areas of the Mössbauer spectra were normalized to the same weight of sample, and corrected for the background contribution of the 122 keV gamma rays from the source, which deposit about 14 keV of their energy in the detector through Compton scattering.

RESULTS

The room temperature spectra (Figure 1) for all samples consist of a strong quadrupole doublet due to ferric ions (splitting $(\Delta) \sim 0.5$ mm/sec) and a weak doublet

due to ferrous ions ($\Delta \sim 2.2$ mm/sec). On cooling a sample of the uncontaminated sediment the spectral area of the ferric doublet was decreased, and a magnetic component appeared that formed about 50% of the total area at 77°K and 4.2°K (Figure 2). The hyperfine field value at 4.2°K of 499 kOe is in better agreement with that expected for goethite, 506 kOe (van der Kraan and van Loef, 1966), than that for $\beta\text{-FeOOH}$, 470 kOe (Hogg *et al.*, 1975). Since no magnetic component in the room temperature spectrum was found, it is likely that the goethite is present as finely divided particles (Shinjo, 1966; van der Kraan and van Loef, 1966; Govaert *et al.*, 1977), although the possibility that it contains some substituted aluminum cannot be ruled out on the basis of the field values (Bigham *et al.*, 1978). A spectrum containing a magnetic component ($\sim 50\%$ of total area) with a field of 386 kOe and an outer linewidth of 1.81 mm/sec was measured at 195°K . Comparison with the corresponding areas measured at other temperatures implies that the blocking temperature lies between 195°K and room temperature. Using an anisotropy constant of 1.5×10^4 erg/cm³ (Shinjo, 1966), a mean volume of the goethite particles of $1\text{--}1.5 \times 10^{-17}$ cm³ can be calculated.

After irrigation of the material for 300 and 750 days, there is an increase of about 30% in the total Mössbauer peak area of the spectra taken at 300°K and 4.2°K , but none for the spectra obtained at 77°K . This anomaly probably reflects the inaccuracy in the area measurements. It is clear, however, that additional magnetic components are present in the 4.2°K spectrum (Figure 3). A better fit is obtained to this spectrum on the basis of two extra magnetic components ($\chi^2 = 288$; $H = 435$ and 470 kOe), than for one extra component ($\chi^2 = 403$; $H = 446$ kOe). The corresponding number of degrees of freedom is 230 and 236, respectively. No extra magnetic components are present in the 77°K spectrum, which again suggests relaxation behavior due to fine particle size. After removal of the 'amorphous oxides,' the total peak area at each temperature was significantly reduced, and the extra magnetic components were absent from the 4.2°K spectrum. In addition, only a very slight reduction in the area due to goethite was noted (Table 3).

Table 3. Component areas in Mössbauer spectra of Lower Greensand.

Days irrigation	300°K		77°K		4.2°K				
	Total area	Total area	Non-magnetic area	Magnetic area	Total area	Non-magnetic area	Magnetic area (1)	Magnetic area (2)	Magnetic area (3)
0	0.8	1.2	0.7	0.5	1.2	0.6	0.6	—	—
300	1.1	1.3	0.8	0.4	1.6	0.5	0.6	0.1	0.4
750	1.0	1.1	0.7	0.4	1.6	0.6	0.7	0.1	0.2
750 ¹	0.7	1.0	0.6	0.4	1.0	0.5	0.5	—	—

Areas reported in arbitrary units.

¹ This sample was chemically treated to remove the amorphous oxide fraction.

Table 4. Mean hyperfine parameters derived from fits to Mössbauer spectra of Lower Greensand.

Temperature	Ferric component			Ferrous component			Magnetic component			
	Δ	δ	Γ	Δ	δ	Γ	H	Q	δ	Γ
300°K	0.574	0.359	0.474	2.210	1.268	0.404	—	—	—	—
77°K	0.572	0.453	0.607	2.722	1.363	0.358	478	0.100	0.494	0.669
4.2°K	0.483	0.461	0.890	2.731	1.756	0.637	499	0.094	0.494	0.577 ¹
							470	0.010	0.520	0.717 ²
							435	0.050	0.549	0.667 ²

Δ = quadrupole splitting; δ = isomer shift relative to α -iron; Γ = half-width; Q = quadrupole shift, all values in mm/sec; H = hyperfine field in kOe.

¹ Components present in all samples.

² Components present only in samples after irrigation.

The remaining ferric doublet in the 4.2°K spectrum and the ferrous doublet at all temperatures can be assigned to iron in glauconite and montmorillonite. Because the concentration of iron in glauconite may be as much as an order of magnitude greater than that in montmorillonite, it is likely that most of these components are due to iron in glauconite.

The spectra for the glauconite sample were fitted to four doublets due to ferric and ferrous ions in octahedral sites; M(1) with hydroxyl groups in trans positions and M(2) with hydroxyl groups in cis positions. Although some doubt has been expressed about the identification of these doublets in Mössbauer spectra (see, e.g., Rozenson and Heller-Kallai, 1978), assignment of the ferric doublets (Table 5) was made on the basis that the ratio of the splittings for M(1) to M(2) sites would be expected to be ~2:1, if the sites are relatively undistorted (Rozenson and Heller-Kallai, 1977, 1978). Although two doublets arising from ferrous ions were included in the fits for the sake of completeness, only the more intense is statistically significant. Separate contributions from M(1) and M(2) sites could not be distinguished in the central ferric doublet of the Lower Greensand spectrum (300°K, Figure 1A) due to the presence of an additional doublet of comparable magnitude and splitting due to fine particle goethite.

The P(H) distributions (Figure 5) derived from the fits to the applied field spectra (Figure 4) all display broad peaks centered at field values of about 80, 350, and 490 kOe. The very small peak at about 650 kOe is spurious and due to fluctuations in the data. The broadness of

each peak reflects a range of internal fields arising from the different vector coupling between the applied and hyperfine fields. The field of 490 kOe may be associated with the goethite component. Additional peaks in distributions B and C (Figure 5) corresponding to the contaminated samples are not apparent, although the strong peak centered at 490 kOe increases in intensity, particularly in B. It is likely, therefore, that the extra components are concealed within this strong peak. The corresponding P(H) distribution for glauconite (curve E in Figure 5) contains broad peaks centered around field values of about 100, 350, and 450 kOe. By measuring the applied field spectrum after intergrade oxide was removed from the sample with sodium dithionite (Follett, 1965), it was shown that the main field at 450 kOe was not due to impurity iron oxide.

Comparison of curve E with those for the sediments (A, B, C, and D) indicates that glauconite is present in the sediments. It is possible that the very low 'field' value of 80–100 kOe is produced as a result of fitting a magnetic spectrum to what is really a quadrupole doublet (splitting ~ 2.5 mm/sec). The fact that internal fields as much as an order of magnitude higher than the applied field are present, indicates paramagnetic behavior for most of the iron ions. The overall spread in fields from about 300–500 kOe is probably due to a range of magnetic moments on the iron ions.

DISCUSSION

The identification of the additional magnetic components present in the 4.2°K spectra for the sediment

Table 5. Hyperfine parameters for glauconite.

Temperature	Ferric components								Ferrous components							
	M(2) cis				M(1) trans				M2 (cis)				M1 (trans)			
	Δ	δ	Γ	Area	Δ	δ	Γ	Area	Δ	δ	Γ	Area	Δ	δ	Γ	Area
300°K	0.486	0.343	0.524	85%	1.126	0.393	0.314	10%	2.196	1.400	0.394	3%	1.690	1.179	0.390	1%
4.2°K	0.560	0.453	0.702	86%	1.282	0.509	0.366	10%	2.306	1.639	0.398	3%	2.036	1.578	0.376	1%

Δ = quadrupole splitting; δ = isomer shift relative to α -iron; Γ = half-width. All values in mm/sec.

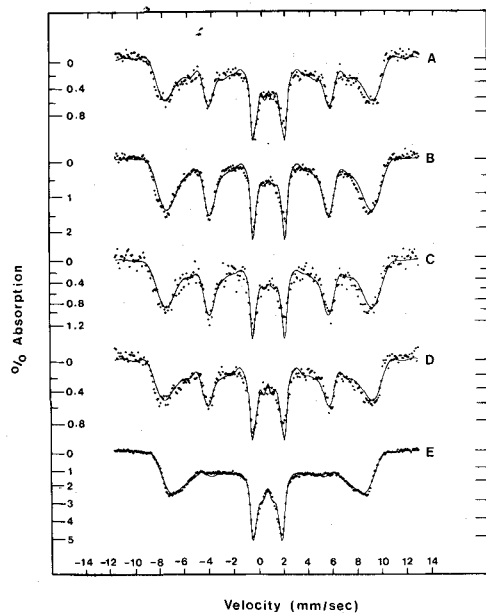


Figure 4. Fe^{57} Mössbauer spectra at 4.2°K for an applied field of 45 kOe parallel to the gamma ray direction; A = original Lower Greensand; B and C = Lower Greensand irrigated for 300 and 750 days; D = Lower Greensand after treatment to remove easily reducible oxide; E = glauconite.

after irrigation is not straightforward, since the field values of 435 and 470 kOe (Table 3) do not correspond to those of any bulk iron oxides except possibly $\gamma\text{-FeOOH}$. Similar spectra were observed by Govaert *et al.* (1977) at higher temperatures (77° and 300°K) for goethite having a defect structure due to the presence of water molecules which reduce the average grain size. These spectra were fitted using a combination of a single hyperfine field for atoms in the grain core and one flank of a Gaussian distribution for atoms in the surface layers. Although Govaert *et al.* (1977) reported no measurements at 4.2°K , the effect of decreasing temperature was to reduce the width of the overall distribution and, hence, to narrow the lines. Such a behavior is not consistent with the 4.2°K spectra for the sediment after irrigation. The additional field values in these spectra, however, are in reasonable agreement with those for either a natural ferric gel (Coe and Readman, 1973) or for synthetic gels (Okamoto *et al.*, 1972; Mathalone *et al.*, 1970). Using the values for the anisotropy energy and the frequency factor derived by Mathalone *et al.* (1970) and assuming a blocking temperature between about 10° and 70°K , an approximate range of particle volumes may be calculated between 1.3 and $9.1 \times 10^{-20} \text{ cm}^3$.

The structure of ferric hydroxide gel is clearly different from that of water-disrupted goethite, and has been characterized by Towe and Bradley (1967) as a loose array of oxygen ions and water forming a hexagonal close-packed lattice (ABAB), enclosing ferric

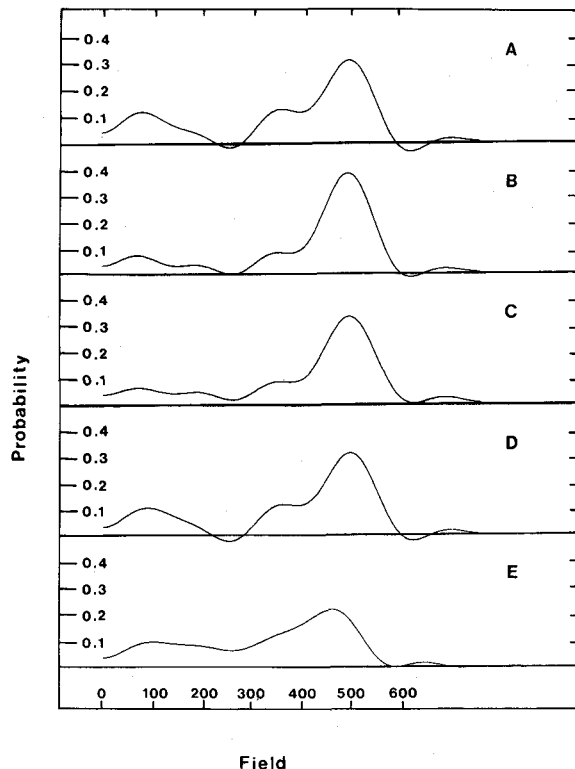


Figure 5. Hyperfine field probability distributions $P(H)$ derived from fits to the spectra at 4.2°K in an applied field of 45 kOe for samples A, original Lower Greensand; B and C, Lower Greensand after irrigation for 300, 750 days; D, after treatment to remove easily reducible oxide; E, glauconite.

ions in the octahedral interstices. This loose structure can readily assimilate larger heavy metals such as Pb^{2+} and Cd^{2+} , which are prevented by steric and size constraints from entering the more rigid goethite lattice.

Chemical extraction data (Table 2) show that lead and cadmium are more strongly associated with the "easily reducible" fraction than with the "moderately reducible" goethite phase (Ross, 1978). Since the "easily reducible" fraction corresponds to the additional magnetic components (Table 3), and the presence of lead and cadmium indicates that the fraction lacks long-range order, the assignment of these components to a gel is reasonable. In addition, the order of retention of heavy metals (Table 2, $\text{Pb} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$) is the same as that found by Kinniburgh (1974) for synthetic ferric gels. This sequence is markedly different for other oxide phases.

The Mössbauer data indicate that the gel has remained stable over the three-year period of irrigation. The slight reduction in the spectral area due to the gel, between 300 and 750 days irrigation (Table 3), may be due to physical migration of the very small particles. Ageing of metal hydroxides may proceed either to a metastable "inactive" form of the same phase, or by

phase transformation to a more stable modification. Feitknecht and Schindler (1963) indicated that amorphous ferric hydroxide may be modified to the active form of goethite or to hematite, the thermodynamically stable α phase. Because of the very fine particle size (and hence large surface area/volume ratio) the dominant control of the stabilities of the different mineralogical phases is probably the free surface energy of the particle (Ferrier, 1966). Langmuir and Whittemore (1972) attributed the continued stability of "amorphous" ferric hydroxide particles of less than 100-Å diameter over periods of more than 1000 years in natural groundwaters to this effect. The stability of the gel phase may also reflect an inhibition of reordering by the structural incorporation of heavy metals, as demonstrated by Nalovic *et al.* (1976).

CONCLUSIONS

This study has indicated the potential of Mössbauer spectroscopy as a tool for phase analysis of fine particle iron compounds in pollution studies. Because iron is sensitive to changes in redox potential, Mössbauer spectroscopy may offer a means of assessing redox conditions in the unsaturated zone by mineralogical facies analysis.

The following conclusions may be drawn from this study:

1. Iron is present in the Lower Greensand in the form of fine particle goethite (α -FeOOH) (volume $\sim 1 \times 10^{-17}$ cm³) and in glauconite and montmorillonite.
2. Irrigation with a heavy metal solution leads to the formation of a ferric hydroxide gel (volume = 10^{-19} – 10^{-20} cm³). There is no evidence for the attenuation of iron in any other form.
3. There is no evidence for the structural transformation of the gel phase during a three-year irrigation period.
4. Glauconite displays paramagnetic behavior in an applied magnetic field, with a wide range of induced hyperfine fields, reflecting a corresponding range of structural positions.

ACKNOWLEDGMENTS

This study was funded in part by the Department of the Environment, under the Landfill Research Programme. It is a pleasure to thank L. W. Becker and K. B. Parnham for technical assistance and M. S. Ridout for the program used to plot the Mössbauer spectra. Glauconite samples were provided by D. J. Morgan, Applied Mineralogy Unit, Institute of Geological Sciences. We also thank J. D. Mather and D. J. Morgan for their critical reading of the manuscript.

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(Received 9 April 1979; accepted 10 September 1979)

Резюме— Fe^{57} Моссбауэровская спектроскопия была использована для определения природы минералов, содержащих железо в образцах Нижнего Зеленого песчаника из экспериментального лизиметра в Аффингтоне, Оксфордшир, перед и после трех-летней ирригации синтетическим раствором тяжелого металла. Анализ спектров, замеренных при 300°, 77°, и 4,2°K и при 4,2°K в поле 45 кОе показывает, что железо присутствует в необработанном песчанике в мелко-зернистом гетите (α -FeOOH) и глауконите. В ирригированных образцах железо осаждается в виде мелко-зернистого железно-гидроокисного геля, имеющего значения для сверхтонкого поля 435 и 470 кОе при 4,2°K. Устойчивость геля в течение трех-летнего периода ирригации можно объяснить, приняв во внимание поверхностную энергию. [N. R.]

Resümee— Fe^{57} Mössbauer-Spektroskopie wurde verwendet, um die eisenhaltigen Minerale in Lower Greensand Proben aus einem Versuchslsylimeter in Uffington, Oxfordshire, zu bestimmen. Die Untersuchung wurde sowohl vor als auch nach einer dreijährigen Irrigation mit einem synthetischen Schwermetallauslaugprodukt durchgeführt. Die Auswertung der Spektren, die bei 300°, 77°, und 4,2°K sowie bei 4,2°K in einem angelegten Feld von 45 kOe gemessen wurden, zeigt, daß das Eisen in nicht verunreinigtem Sandstein in Form von feinkörnigem Goethit (α -FeOOH) und Glaukonit vorhanden ist. In den verunreinigten Proben ist das Eisen als feinkörniges Fe^{3+} -Hydroxydgel gefällt, das für das Hyperfeinfeld Werte von 435 und 470 kOe bei 4,2°K hat. Die Stabilität des Gels über einen dreijährigen Zeitraum der Irrigation kann durch Überlegungen über die Oberflächenenergie erklärt werden. [U. W.]

Résumé—La spectroscopie Mössbauer Fe^{57} a été utilisée pour déterminer la nature de minéraux contenant du fer provenant d'échantillons de Bas Greensand d'un lysimètre expérimental à Uffington, Oxfordshire, à la fois avant et après une irrigation de trois années avec un lourd lessivant synthétique. L'analyse des spectres mesurés à 300°, 77°, et 4,2°K et à 4,2°K dans un champ appliqué à 4,5 kOe montre que le fer est présent dans le grès non-contaminé dans la goethite à fins grains (α -FeOOH) et dans la glauconite. Dans les échantillons irrigés, le fer est précipité comme un gel hydroxide ferrique à fins grains ayant pour le champ hyperfin les valeurs 435 et 470 kOe à 4,2°K. La stabilité du gel pendant une période de trois ans peut être expliqué par des considérations d'énergie de surface. [D. J.]