



## Mössbauer Observation of the Mobility of Cl<sup>-</sup> Ions in a Frozen Solution

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Samples of fly-ash from the Yallourn Power Station were treated with HCl and FeS<sub>2</sub> at temperatures up to 200 °C to enable the extraction of Mg and Fe. The valency distribution of the Fe in the eluent was determined by Mössbauer spectroscopy at 193 K. Although well below the freezing temperature, the subspectra of the ferrous components due to [FeCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] and [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> changed continuously with time due to migration of the Cl<sup>-</sup> ions.

### 1. Introduction

When an aqueous solution liquid is frozen, the crystallographic arrangement of the frozen material depends on the speed of freezing. We usually then consider that, once frozen, they remain unchanged unless allowed to come up to near their melting or eutectic point. Since the earliest days of Mössbauer spectroscopy, there have been studies of various frozen solutions and viscous liquids aimed at understanding the dynamics of the recoilless fraction, the atomic arrangements in frozen solutions, diffusion magnetic relaxation and the effects of the speed of freezing to name but a few [1].

The starting material was fly-ash from the electrostatic precipitator of Energy Australia's Yallourn brown coal power station in Victoria. The ash had previously been part of an extensive set of investigations, including by Mössbauer spectroscopy [2] as part of a wide survey by the then State Electricity Commission of Victoria of all existing and potential brown coal fields and their products. The principal chemical elements in Victorian coal ash are Fe, Mg, Ca and Al, in varying proportions, with the most common phases being the spinel phase aluminium-substituted magnesioferrite, MgFe<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub>, or the brownmillerite structure calcium aluminoferrite, Ca<sub>2</sub>Fe<sub>2-x</sub>Al<sub>x</sub>O<sub>5</sub> along with periclase, MgO, CaSO<sub>4</sub> and other smaller constituents. In the search then for potential uses for the various fly-ash by-products, a high Ca content made it attractive as a cement extender.

However, there is recent interest in the use of alkaline earths for mineral carbonation as a promising technology for the permanent capture of anthropogenic CO<sub>2</sub> [3,4,5]. The source of the alkaline earths can be fly-ash, steelmaking slag or natural minerals, but the operating conditions can be severe. A potentially easier route for carbonation is to first leach out the alkaline earths, which must also be contaminant free. There has been little investigation of the leaching of industrial wastes, particularly involving the mobilization of Fe, with each material requiring individual evaluation.

### 2. Sample preparation

The principal form of both Fe and Mg in Yallourn fly-ash is as magnesioferrite. Hence any leaching of the Mg will inevitably result in some mobilization of Fe as well. An initial leaching of the fly-ash using 2M HCl for 5 min at room temperature was carried out to remove simple oxides and this became the feedstock for subsequent experiments. The first of these involved 2M HCl at temperatures of 20 °C, 100 °C and 200 °C. Three more leachings were carried out using sulphur compounds as a reductant, at the same three temperatures. The sulphur compounds used were sodium sulphide, Na<sub>2</sub>S.9H<sub>2</sub>O, sodium dithionite Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and pyrite, FeS<sub>2</sub>, which may indicate how the sulphur inherent in the fly-ash may behave. The



solid products were examined by XRF, ICP-OES, XRD, Mössbauer spectroscopy and both K-edge Fe and K-edge S XANES. Further details of these experiments may be found in ref. [6].

It was of particular interest to determine the valence of the iron species in the eluent since the solid starting material was entirely ferric, so Mössbauer spectra were taken of frozen solutions of the HCl leached eluent and the FeS<sub>2</sub> leached eluent. Approximately 1 mL of the samples was sealed into perspex absorber holders leaving a small air space to allow for expansion on freezing. They were then placed flat in a container of liquid nitrogen and thermal equilibrium attained in approximately two seconds. Because it was expected that each experiment would need about a week to run, it was decided on economical grounds to use dry ice as the refrigerant so the samples were allowed to come to thermal equilibrium with the 193 K temperature of dry ice.

### 3. Results

The sample from the FeS<sub>2</sub> leaching was run first and the spectra were saved each day. It soon became apparent that the spectrum was changing with time. The final spectrum is shown in Fig. 1b with the fit to two ferrous doublets (green and red lines) and one ferric doublet (light blue). The ferrous doublets are well-defined but the ferric doublet is very broad as will be discussed in the next section. The spectrum of the HCl leached sample is shown in Fig. 1a. It can be seen that it is not as well defined as the previous spectrum and the dip only one-quarter the size. This, coupled with the smaller proportion of the spectrum being ferrous, made the day-by-day difference spectra too poor to be sure whether there was a significant change in the ferrous doublets. The spectrum has been fitted to the same model as Fig. 1b and the parameters for both fits are given in Table 1.

Fig. 2 shows the spectra for each day for the FeS<sub>2</sub> sample obtained by subtracting each day's starting spectrum from that saved on the succeeding day. Although the statistics are not exceptional because each is time limited, it is clear that there is a continual change in the spectrum. The spectrum for the first day has a smaller percentage absorption than succeeding days. It can also be seen that the splitting of the outer doublet is smaller than the splitting for the succeeding days and also there is poorer definition of the peaks with apparently some additional absorption in the region between the respective peaks of the two ferrous doublets. By the second day we can see a big increase in the absorption of the inner doublet. However, by days 3-5 we see a continual increase in the absorption of the outer doublet at the expense of the inner one. The parameters for the fits are also in Table 1.

Table 1. Fitted parameters for the spectra in Figs. 1 and 2.

Sample	Day	Outer Ferrous Doublet			Inner Ferrous Doublet			Ferric Doublet		
		$\delta$ (mm/s)	$\Delta$ (mm/s)	Area (%)	$\delta$ (mm/s)	$\Delta$ (mm/s)	Area (%)	$\delta$ (mm/s)	$\Delta^*$ (mm/s)	Area (%)
HCl		1.29(6)	3.14(1)	15	1.35(2)	1.59(5)	30	0.40(5)	0.0(10)	55
FeS <sub>2</sub>	1	1.33(4)	2.95(9)	42	1.33(2)	1.55(5)	36	0.24(54)	0.9(16)	22
	2	1.27(2)	3.17(4)	18	1.34(5)	1.59(1)	67	0.24(16)	0.4(10)	15
	3	1.27(1)	3.17(2)	32	1.34(6)	1.59(1)	53	0.21(19)	0.0(13)	15
	4	1.26(1)	3.16(1)	38	1.33(5)	1.60(1)	43	0.29(10)	0.5(11)	19
	5	1.27(1)	3.16(1)	48	1.34(1)	1.60(2)	28	0.41(8)	0.0(10)	24
	total	1.27(1)	3.16(1)	36	1.34(1)	1.60(1)	45	0.31(5)	0.0(13)	19

$\delta$  is the isomer shift,  $\Delta$  is the quadrupole splitting, the number in parentheses is the uncertainty in the last digit.

\* The listed uncertainty is the standard deviation of the fitted quadrupole splitting distribution (see text).

### 4. Interpretations and Discussion

The parameters of the outer ferrous doublet agree well with those of crystalline FeCl<sub>2</sub>·6H<sub>2</sub>O [7] for which the iron entity is trans-[FeCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]. This has also been observed

in previous experiments on frozen  $\text{FeCl}_2$  solutions [8]. The inner doublet is also well-characterized as being due to the more symmetrical  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . Previous experiments [7] have shown that these doublets can transform to the other under change of temperature, but we believe that this is the first observation of such a change as function of time at constant temperature. The transformation involves the migration of two  $\text{Cl}^-$  ions into the inner coordination sphere. The poorly resolved spectrum at Day 1 indicates that there was considerable movement going on, with this having a detrimental effect on the recoilless fraction of both sites. The two doublet fit with broad lines is almost certainly not a true representation of the physical picture as it would appear that there is some evidence for an intermediate  $[\text{FeCl}(\text{H}_2\text{O})_5]^+$  configuration, so that the ratio of the two sites for Day 1 probably has little validity. After this, the ratio of the outer to inner site areas changed from 0.26:1 to 1.7:1 over the next 4 days as the sample aged at 193 K.

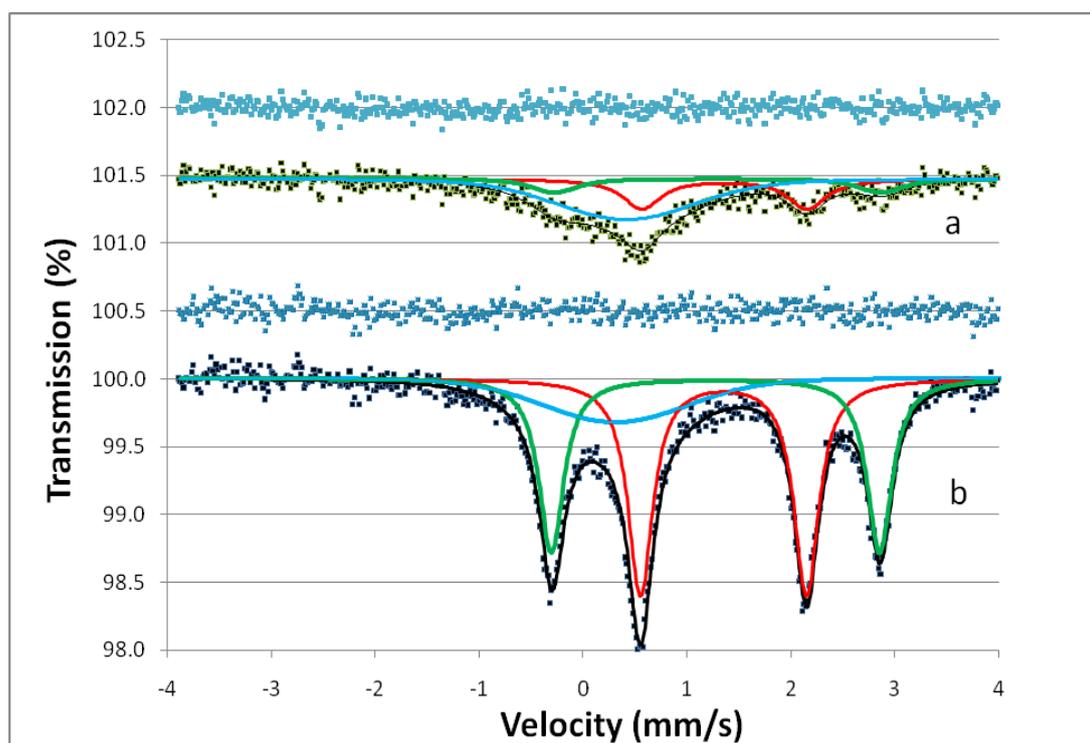


Fig. 1. Mössbauer spectrum of (a) the frozen eluent from the sample leached with 2M HCl, and (b) the sample reduced with  $\text{FeS}_2$ . The blue lines above each spectrum are the difference between the data and the fit.

The very broad ferric doublet made the fitting of Fig. 1(a) subject to considerable statistical error. The broadness can vary considerably, dependent on concentration, [8]. It always has a decidedly non-Lorentzian shape due to spin-spin relaxation, as studied in detail in ref [10]. However, with no resolvable features on this subspectrum to fit to a relaxation model, we have used Voigtian lineshapes with a quadrupole split distribution to enable a good fit to the data, and hence estimation of the area, to be obtained.

There is clearly an increase in area between the Day 1 and Day 2 spectra in Fig. 2, so we cannot strictly treat the recoilless fraction as a constant. We note that the ratio of the areas of Fig. 1(b) to Fig. 1(a) is 3:1 although the ratio of the concentrations is only 1.6:1. The main concern about this discrepancy is the effect that it may have on the ferrous/ferric ratio derived from the areas. XANES measurements of the sample [6] gave 19% ferric for the  $\text{FeS}_2$  sample, in exact agreement with our average value, and 65%  $\text{Fe}^{3+}$  for the HCl sample compared to our 55%. These are in satisfactory agreement, given the uncertainties.

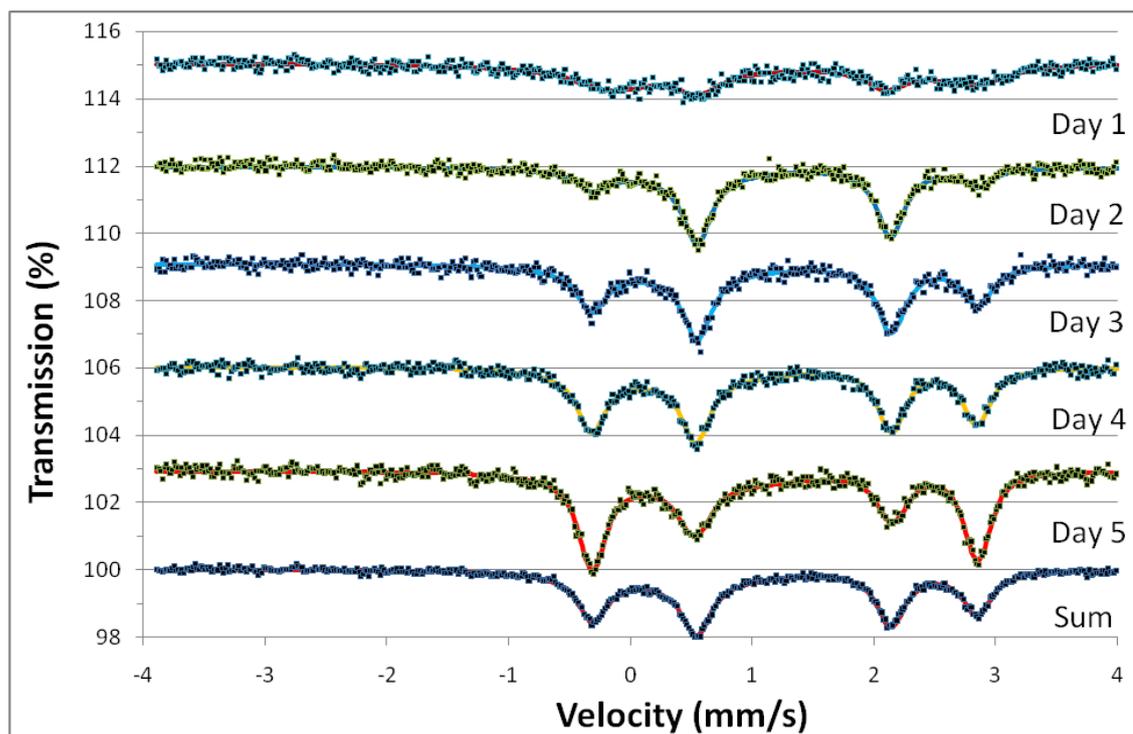


Fig. 2. Mössbauer spectra of the FeS<sub>2</sub> reduced sample as a function of time.

#### 4. Conclusions

It is rare in Mössbauer Spectroscopy to be able to follow physical or chemical transformations in real time, but here we have been able to observe the effect of Cl<sup>-</sup> migration at 193 K in a frozen solution of FeCl<sub>2</sub> in 2M HCl as the Fe<sup>2+</sup> changes coordination from [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> to [FeCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].

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