

## MÖSSBAUER STUDY OF GOLD SORPTION ON POLYURETHANE FOAMS

W.H. JAY<sup>1</sup>, J.D. CASHION<sup>2</sup> and L.J. BROWN<sup>2</sup>

<sup>1</sup>*Department of Chemical Engineering, Monash University, Clayton, Vic. 3168, Australia*

<sup>2</sup>*Department of Physics, Monash University, Clayton, Vic. 3168, Australia*

Gold sorbed onto different types of flexible polyurethane foams from cyanide solution at pH 11 is shown to remain as the  $\text{Au}(\text{CN})_2^-$  ion. At least two different bonding mechanisms occur, with different recoilless fractions, and possible configurations are suggested.

### 1. INTRODUCTION.

The majority of gold extraction from commercial gold ores is carried out by the adsorption of the gold from cyanide solution onto activated carbon at approximately pH 10. The gold is subsequently eluted, usually with a dilute solution of  $\text{NaCN}/\text{NaOH}$ . The main aspects of this adsorption have been established only recently, with Mössbauer spectroscopy providing the most direct evidence that the adsorbed species is the  $\text{Au}(\text{CN})_2^-$  ion [1-4].

Flexible polyurethane foams can also sorb anionic species [5] and the present knowledge is summarised in the review by Braun [6] and references therein. The possible substitution of polyurethane foams for activated carbon in gold extraction plants has two potential advantages. The first is the greatly enhanced loading kinetics because of the more open structure, while the second is the possible use of solvents other than cyanide to extract gold from the ores.

In this paper we present the first Mössbauer experiments on the sorption of gold from cyanide solution onto several different types of polyurethane foams.

### 2. EXPERIMENTAL DETAILS

Ten different polyurethane foams were selected to cover a range of types as detailed in Table 1. A 5g sample of each foam was washed in 500ml of 1N nitric acid, then repeatedly washed in distilled water. Crystalline  $\text{KAu}(\text{CN})_2$  (Johnson Matthey) was dissolved in distilled water to make a 1000ppm solution and the pH adjusted to 11 with  $\text{NaOH}$ . The foam was immersed in the solution for four hours with continuous bubbled air and occasional squeezing. The wet foam was compressed in a 7cm aluminium tube, the amount varying from 2.5g to 4g, and maintained frozen until required. The gold loading was determined by atomic absorption.

The source used was 80mg of isotopically enriched (96%)  $^{198}\text{Pt}$  metal, irradiated in the A.N.S.T.O. HIFAR reactor for 12h at  $5 \times 10^{13}$  n/cm<sup>2</sup>/s. All spectra were taken with both the source and absorber in an exchange gas space in a liquid helium cryostat at a nominal temperature of 4.2 K. The spectra have been fitted with Lorentzian lineshapes with the two lines of a doublet not always constrained to have equal intensities to test for the existence of the Goldanskii-Karyagin effect. The isomer shifts are quoted with respect to gold metal.

### 3. RESULTS

Two of the Mössbauer spectra obtained are shown in Fig. 1 and are principally doublets with parameters appropriate for the  $\text{Au}(\text{CN})_2^-$  ion. However, all the spectra were of very low intensity, typically 0.1-0.2% absorption, compared to dips of up to 3% obtained with  $\text{Au}(\text{CN})_2^-$  adsorbed onto activated carbon. This consequent poor signal to noise ratio made it difficult to draw definite conclusions about possible deviations of the absorption dip from being simple symmetrical doublets. However some features are discernable in the spectra. For example, in

the spectrum of foam 1 (Fig. 1a), a doublet has been fitted although the left hand peak seems to be appreciably wider than the right hand peak. We are unable to justify physically alternative choices of fitted lines.

The spectrum of foam<sub>6</sub> in Fig. 1b shows the clearest case where the left hand peak is composed of two separate members, and if only fitted to one doublet the parameters are markedly different from those of all the other samples. The linewidth values of the spectra have a very low accuracy but vary from 1.9–2.5 mm/s compared to the natural linewidth ( $2\Gamma$ ) of 1.88 mm/s and typical results for  $\text{Au}(\text{CN})_2^-$  on activated carbon /2–4/ of 2.0–2.1 mm/s. Foams 8 and 9 gave markedly broadened spectra.

A separate  $^{119}\text{Sn}$  Mössbauer spectrum has been taken of foam 1, which has a tin catalyst incorporated as tin(II) octoate (tin(II) 2-ethylhexanoate). However the spectrum shows that the tin is principally present as a tin(IV) species with an isomer shift close to zero and a small unresolved quadrupole splitting very similar to the parameters of  $\text{SnO}_2$  and many other related species. A very small doublet ascribable to unreacted tin(II) octoate was also discernable.

#### 4. INTERPRETATIONS

The isomer shift and quadrupole splitting values all fall within a very narrow range and are very close to those already observed for the  $\text{Au}(\text{CN})_2^-$  species. Fig. 3 shows a correlation plot for the quadrupole splitting against the isomer shift for all  $\text{Au}(\text{CN})_2^-$  species. It can be seen that the results fall into three distinct groups, namely the crystalline and frozen solution samples, adsorbed species on activated carbon and now sorbed species on polyurethane foam with the last group having the largest s-electron density. A linear relation in plots such as Fig. 3 implies a constant hybridization ratio between the electrons involved in bonding, principally 6s and 6p electrons in this case. However, the relation appears to be flattening out with the polyurethane foam samples, suggesting that this is no longer the case.

In Fig. 2 the ratio of the percentage area of the absorption to the mass of adsorbed gold in the sample (which is directly proportional to the recoilless fraction), has been plotted against the mass ratio of sorbed gold to foam. The non-linear nature of this plot shows that either the different foams have different strengths of binding for the  $\text{Au}(\text{CN})_2^-$  ion or that the initial, and

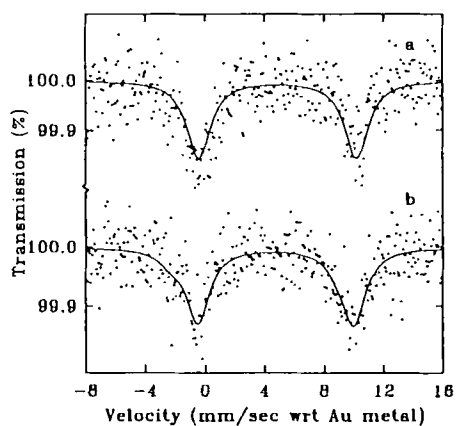


Fig. 1.  $^{197}\text{Au}$  Mössbauer spectrum of (a) foam 1 and (b) foam 6 at 4.2 K.

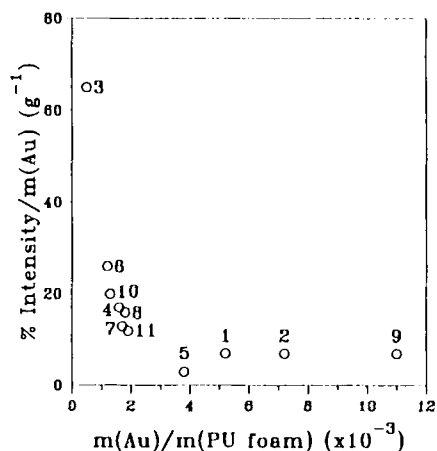


Fig. 2. Plot of normalized spectral area against gold loading for the foam samples.

Table 1. Details of the polyurethane foams used.

Foam no.	Polyol RMM	Water pphp <sup>1</sup>	R11 <sup>2</sup> pphp	Parts <sup>3</sup> EO to 100 PO	MDI/TDI	Urea cont.	Tin <sup>4</sup> cat.	Manuf.	Note
1	3800	4.5	5	-12	TDI	med.	yes	DOW	
2	3800	4.5	5	-12	TDI	med.	no	DOW	(a)
3	3000	5.0	10	0	TDI	high	yes	DOW	
4	3000	4.0	20	0	TDI	low	yes	DOW	(b)
5	3000	2.0	nil	0	TDI	v. low	yes	DOW	(b)
6	4800	3.0	nil	-20 <sup>5</sup>	MDI	high	no	URECEL	
7	4800	nil	30	-20 <sup>5</sup>	MDI	low	no	URECEL	(c)
8	4800	3.5	nil	-20 <sup>5</sup>	MDI	high	no	URECEL	(d)
9	5000	3.5	15-20	150 <sup>6</sup>	TDI	n.a.	yes	DUNLOP	(e)
10	3000	2.5	nil	<5	TDI	low	yes	DOW	(f)
11	3000	2.0	nil	0	TDI	low	yes	DOW	(g)

1 pphp – parts per hundred parts polyol.

2 R11 – trichloro monofluoro methane.

3 EO – ethylene oxide, PO – propylene oxide.

4 catalyst as tin(II) 2-ethylhexanoate. All have amine catalyst.

5 polyol tipped with EO to give approx. 75% of terminal OH groups.

6 approximate parts EO to 100 PO in polyol.

(a) Same as foam 1 but without tin catalyst.

(b) Same as foam 3 but with less water to reduce urea content.

(c) Same as foam 6 but with no water to reduce urea content.

(d) Same as foam 6 but with 12½% melamine.

(e) Hydrophilic foam.

(f) Contains 40% polystyrene-acrylonitrile interpenetrating polymer as filler.

(g) Contains 10 parts Fyrol CEF (tribetachloroethyl phosphate) fire retardant.

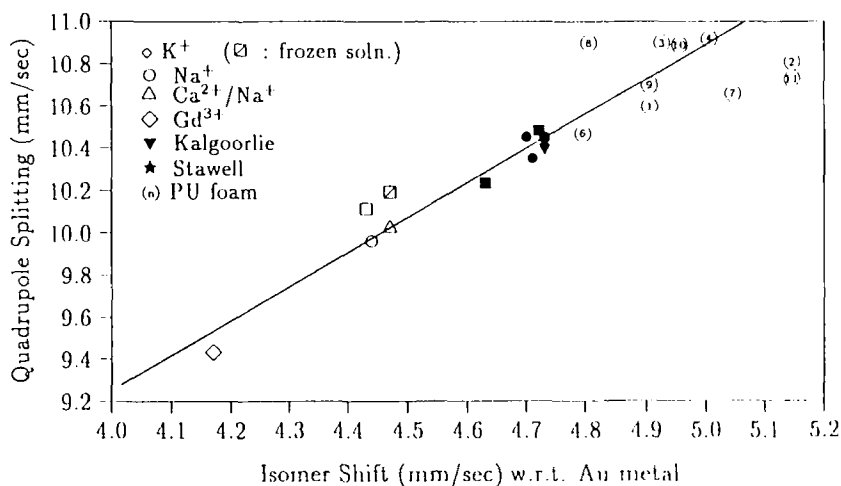


Fig. 3. Correlation plot of quadrupole splitting against isomer shift for cyanide samples. Note the grouping into crystalline samples (open symbols), activated carbon samples (filled symbols) and polyurethane foam samples (numbered circles).

hence preferred, binding sites are more strongly bonded than the sites which have enabled some foams to achieve much higher loadings. These latter sites are presumably not present, or only weakly present, in the other foams.

By comparing the foams in pairs we can draw the following conclusions. The tin catalyst (foams 1 and 2) reduces the amount of gold sorbed and produces possibly the only significant change in the hyperfine parameters, but the strength of the bonding appears unaltered. Since the main effect of the tin catalyst is to promote the gelling reaction, it is expected that foam 2 has an appreciably larger surface area and thus will sorb more gold. The  $\text{Au}(\text{CN})_2^-$  ions may be sorbed both on the surface and inside the foam and the observed difference in the hyperfine parameters could be due to an enhanced surface contribution.

A high urea content (foams 3 and 6 compared with 4,5 and 7 respectively) acts to reduce the mass sorbed although the bonding is considerably stronger. The MDI based foams (6, 7, 8) do not appear to be significantly different from the TDI foams although the MDI foams also differ by having an EO tipped polyol. The addition of melamine appeared to have little effect. The hydrophilic foam clearly has the most outstanding sorption characteristics with the presence of ethylene oxide being a common feature of the foams with high loading. The addition of a filler or a fire retardant appeared to reduce the total sorption, presumably due to a reduced number of available sites, and possibly also reduces the strength of the bonding.

From these comparisons, it is surmised that there are at least two sorption mechanisms in operation. The site in the high urea foams with the higher recoilless fraction probably acts via hydrogen bonding from the cyanide nitrogen to a nitrogen in the chain backbone of the foam. It is possible that there is some mechanical assistance to hindering the amplitude of vibration of the sorbed molecule such as the helical conformations surrounding complexed cations as suggested by Hamon et al./7/. The site with the lower recoilless fraction may operate via hydrogen bonding, involving water molecules at least in the hydrophilic foam, or van der Waals forces, in both cases to a hydroxyl group or ether oxygen atom in the foam. The movement in the isomer shift compared to the activated carbon samples (Fig. 3) may indicate an increased bonding directly at the gold atom. Within the foam group there is evidence for an increased isomer shift with decreasing urea levels.

If the results for  $\text{Au}(\text{CN})_2^-$  on activated carbon were to be plotted onto Fig. 2, then the approximate values would be  $x = 70 \times 10^{-3}$ ,  $y = 7.5$ . Thus the strength of the bonding as represented by the ordinate is the same as for the higher loading foams, suggesting a similar mechanism is involved. The relative loading on activated carbon is over six times as great, but it should be remembered that it is unlikely that we have accidentally found the optimum foam composition, and secondly that the typical loading achieved onto activated carbon in commercial gold extraction plants is approximately 0.003 g gold/g carbon and this figure can be obtained very rapidly with four of the present foams.

## 5. CONCLUSIONS

The sorption of gold from cyanide solution at pH 11 onto polyurethane foams is as the  $\text{Au}(\text{CN})_2^-$  ion. The loading appears to be enhanced by a reduced gelling action, low urea content and the use of a polyol which contains ethylene oxide.

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