

electrodes previously described⁴. With these electrodes, $5 \times 10^{-4} N$ solutions of lead, thallium, cadmium and zinc ions were investigated, by means of cyclic polarization of the electrode, using different rates of voltage sweep and recording the corresponding voltammetric and oscillographic curves.

It was confirmed that the presence of gold in the electrode greatly influences the electrode processes of zinc. Fig. 1a shows the cyclic voltammetric curves for zinc on the 0.1 per cent gold amalgam electrode (curve 1) and on a mercury electrode (curve 2). They differ significantly in both cathodizing and in anodizing.

On gold amalgam the cathodic process is shifted about 20 mV. towards more positive potentials compared with a pure mercury electrode. The differences in the anodic processes are even more pronounced. Zinc is not oxidized at the reversible potential (about -1.0 V.), which is caused by the formation in mercury of a compound, AuZn, that can be oxidized at more positive potentials. A similar effect can be observed even with less concentrated amalgams. Fig. 1c shows the oscillographic curves for zinc at a frequency of 4 c./s. when the exposure was 30 sec. and the concentration of gold in the amalgam is 0.01 per cent. The more pronounced effect is seen in Fig. 1b, where the voltage sweep was 0.3 V./sec. It is evident that both the reduction current for zinc ions, and the oxidation current of zinc from the amalgam, decrease with time when the compound AuZn is formed. This does not occur with the pure mercury electrode. The influence of gold can be neglected only when its concentration in the amalgam is less than 0.001 per cent.

Similar effects were observed for cadmium, although the intermetallic compound AuCd is not so stable as AuZn. Its formation can be observed when the concentration of gold exceeds 0.01 per cent. No influence of gold on the electrode processes of lead and thallium was found.

Those experiments show clearly that the use of gold or gold-plated wires for suspending the mercury drop can give erratic results if the formation of intermetallic compounds is neglected.

On the other hand, our technique for preparing hanging-mercury drop electrodes does not suffer from this difficulty.

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Carbonate Minerals in Hydrated Portland Cement

ALTHOUGH the physical effects of the carbonation of hydrated cements and mortars have been studied¹⁻³, the way in which the carbon dioxide is held has not yet been clearly established. Most workers have

assumed that it exists in the form of calcite; but in work at this Division^{3,4} and elsewhere⁵ the quantity of calcite detected by X-ray diffraction and differential thermal methods is always much less than the amount of carbon dioxide recoverable from the samples. We have investigated this problem in some detail using samples of mortar and carbonated calcium silicate hydrate.

From a study of the X-ray diffraction patterns of the materials before and after carbonation, using a Guinier-type focusing camera of high dispersion, we have concluded that the carbon dioxide is chemically bound as calcium carbonate largely in the form of poorly crystallized vaterite, aragonite and calcite. These minerals have three-dimensional lattices; this does not support the suggestion of Gaze and Robertson⁵, based on indirect evidence, that the carbon dioxide in carbonated tobermorite could be present as two-dimensional calcite. Our results also show that well-crystallized calcite is present in small quantities, but that its amount is not greatly increased by carbonation. In the past, X-ray analyses have determined the amount of this well-crystallized calcite, rather than the amount of the less easily detected poorly crystalline forms now proved to be present, and so have failed to account for all the carbon dioxide found in carbonated mortars.

Other workers¹⁻³ have shown, and we confirm, that the calcium carbonate minerals have formed both from the decomposition of hydrated cement minerals and from calcium hydroxide produced during the hydration of $3\text{CaO} \cdot \text{SiO}_2$ (alite) to $x\text{CaO} \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O}$ in the setting of the cement. As a result they are intimately associated with a siliceous residue with which they readily react on heating. In differential thermal analysis the decomposition of the poorly crystallized calcite produces only a slight endothermic effect (at about 700°C .) and its reaction with the siliceous residue to form larnite ($\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$) is not exothermic. Therefore this method, too, gives little or no indication of carbon dioxide minerals other than well-crystallized calcite (strong endothermic effect at about 850°C .) in carbonated mortars.

Since carbonation of mortars requires the presence of moisture¹⁻³, we suggest that the process takes place through the action of carbonic acid on cement minerals yielding poorly crystallized vaterite, aragonite and calcite in the following manner: Cement minerals \rightarrow siliceous residue + calcium hydroxide \rightarrow vaterite + aragonite + poorly crystallized calcite \rightarrow well-crystallized calcite.

A more detailed account of the investigation will be published elsewhere.

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