

### On the Role of the Electronic Bulk Properties of Semiconducting Minerals in their Interaction with Electrolytes

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The presence of small amounts of copper in galena-electrolyte systems leads to similar effects as those which can be ascribed to variations in the bulk electronic properties of semiconducting minerals. It is shown how trace amounts of copper can influence reproducibly the dissolution rate, the electrical polarizability and the rest potential of galena.

The solid-state properties of semiconducting natural minerals have often been considered to influence their interactions with electrolytes, although the importance of these properties in this context has never been unequivocally established. For instance, differences in semiconducting properties have been proposed by Paul *et al.* [1] to be responsible for observed variations in the electrochemical behaviour of natural galena, whereas Springer [2] had not found an influence of electronic conduction properties in pyrite, chalcopyrite, and galena on their electrical polarization behaviour. Simkovich [3], and Madeley and Boorman [4] observed that the point-defect structure of grown, heavily doped

minerals appreciably effect their flotation behaviour, whereas Gamboa *et al.* [5] found no such influence with synthetic galena.

Such disagreement is perhaps not too surprising, since it can easily be overlooked that the structure of the double layer at a mineral-electrolyte interface, not only depends on the bulk properties of the solid, but is also extremely sensitive to contamination from the ambient. For synthetic semiconductors this was shown by Boddy and Brattain [6], who described the effect of traces of cupric ion on the electrical characteristics of the germanium-electrolyte interface. Further, Larrabee [7] concluded from radioactive tracer studies of the adsorption of metal ions on the compound semiconductors GaAs and InSb that traces of those elements, the electrochemical potential of which, in solution, is more positive than the potential at the semiconductor surface, will be deposited irreversibly at that surface.

We found that also with natural galena (*n* type,  $5 \cdot 10^{-5} \Omega\text{m}$ ), trace amounts of impurities which were not originally present in the material could cause considerable changes to its reactivity. Furthermore, when low levels of certain contaminants were introduced, similar or identical effects could be observed that had been attributed by other workers to variations in the electronic bulk properties of semiconductors. Specifically it was found that traces of copper have an appreciable influence on (a) dissolution rates, (b) electrical polarization, and (c) the electrochemical potential of galena.

#### A. Non-oxidative dissolution

Simkovich and Wagner [8] found that the dissolution kinetics of grown stoichiometric, non-stoichiometric, and heavily Ag- or Bi-doped lead sulphide

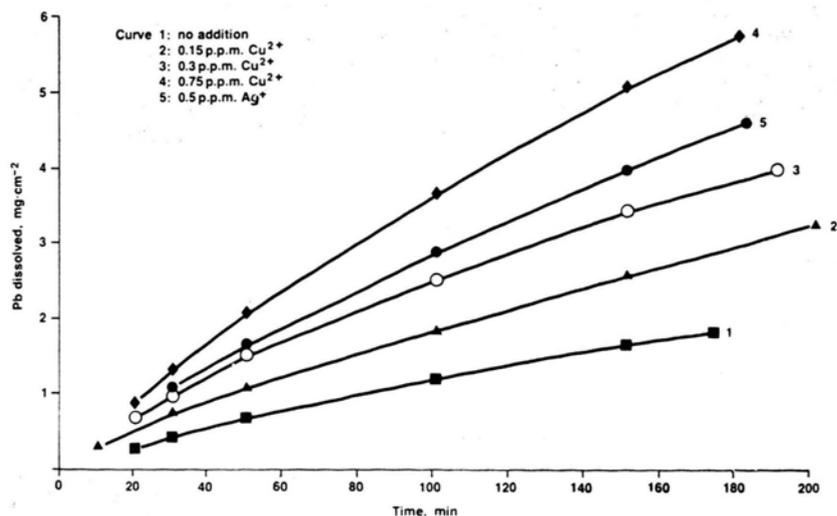


Fig. 1. Dissolution of galena in 2.5 N HCl.

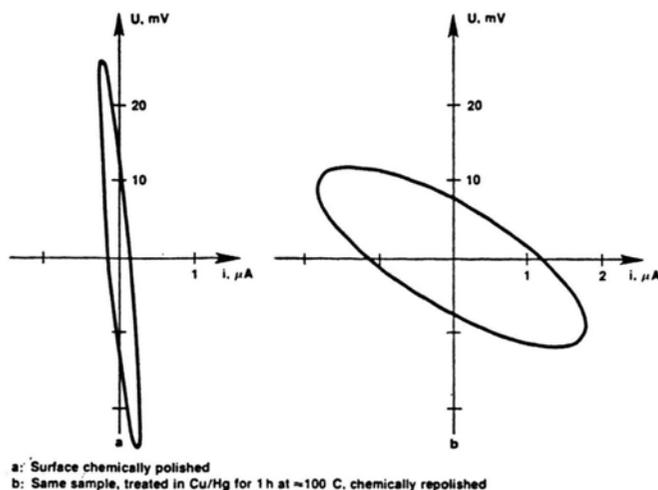


Fig. 2. Polarization traces of galena surfaces at frequency  $f = 5 \times 10^{-2} \cdot s^{-1}$ .

varied markedly with the point-defect concentration of the solid. However, we found that traces of impurities present in the solvent can lead to similar effects. Fig. 1 shows how traces of cupric and silver ion enhance the non-oxidative dissolution of a rotated (200 r/min) galena disc in 2.5 N hydrochloric acid at room temperature.

### B. Electrical polarizability

We found that the polarizability of natural galena surfaces could be drastically changed by bringing them into contact with copper-containing mercury, whereas contact with pure mercury had no effect.

Immersion of the electrode surface into the former for several days at room temperature, or for hours at 100 °C, resulted in a considerable decrease in its polarizability (Fig. 2). By chemical polishing this effect could only gradually be removed, indicating diffusion of copper into the material. This appears feasible, since according to Bloem and Kröger [9], the diffusion coefficient of copper in PbS at 100 °C is of the order of  $10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ .

It is of interest to note that a corresponding decrease in polarizability was observed after a period of 6 years with a galena electrode that had, for electrical contact, a mercury pool at the back of the electrode.

This is a specific example of how uncontrolled diffusion of an impurity from contacts into the solid can change the original solid-state properties. It stresses the validity of the general recommendations given by Peters [10], regarding electrical contacts to natural minerals.

### C. Electrode potential

Gutiérrez and López [11] were the first to correlate measured variations in the rest potential of lead sulphide to its bulk conductivity type and degree of non-stoichiometry. However, we found that changes in rest potential can also result from contamination of the interface by impurities in the electrolyte. As did Boddy and Brattain [6], who reported the change in electrode potential of germanium *versus* time in the presence of traces of cupric ion in solution, we found that the presence of small

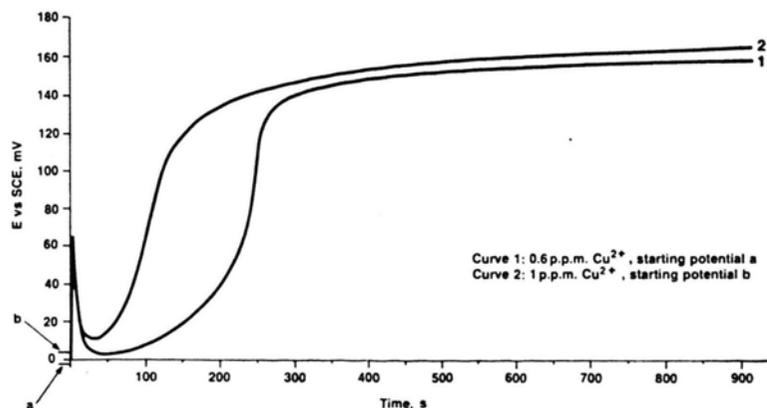


Fig. 3. Rest potentials of galena electrodes, after addition of  $\text{Cu}^{2+}$ . Galena surfaces etched in 2.5 N HCl. Electrolyte 0.3 N HCl in 0.1 M NaCl, magnetically stirred, room temperature.

amounts of cupric ion in solution changed, in a systematic way, the potential of galena electrodes. However, in contrast to Boddy and Brattain [6], who found that the potential of germanium increased at a steadily decreasing rate, we observed a rather different time dependence of the potential for galena. This is shown in Fig. 3. After the addition of cupric ion, the change in potential is characterized by a fast initial rise and decline. This is followed by a second slow increase resulting in an S-shaped potential-time trace. In chloride and perchlorate media this general behaviour was found to be quite reproducible, but dependent in its details on electrolyte concentration and pH value, stirring speed,  $\text{Cu}^{2+}$  concentration, and surface preparation.

In conclusion, it appears that, because of the sensitivity of the mineral-electrolyte interface to contamination, an important consideration in studying the effects of electronic bulk properties of

minerals on solid-liquid interactions must be to establish whether measured effects are due to electronic bulk properties, or to secondary influences, or to both. Especially with heavily-doped materials, the dissolution of impurities might result in contamination levels in the electrolyte high enough to influence interfacial conditions. Such levels of contamination are particularly likely in the plant operation of flotation and leaching processes, when effects due to bulk properties of minerals may easily be masked or overridden by the influence of external impurities.

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