SOLUBILITY OF SILICA IN BASIC ORGANIC SOLVENT SYSTEM

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The release of petroliferous organic compounds contained in Green River oil shale can be affected only after breakdown of the entrapped mineral matrix, predominantly dolomite ($CaMg(CO_3)_2$) and quartz (SiO_2) (1). Dolomite is readily solubilized in an acid medium, but removal of quartz presents a problem. On previous occasions it had been noted that during distillation, potassium hydroxide (KOH) pellets in boiling pyridine dissolved through a Pyrex flask, suggesting that basic organic solvents with potassium hydroxide may serve as good silica solvents.

Experiments were designed to test the solubility of quartz in several solvent systems, prepared as follows:

1) 200 ml quinoline plus 60 g potassium hydroxide pellets added directly.

2) 100 ml quinoline plus 100 ml saturated aqueous potassium hydroxide.

3) 200 ml pyridine plus 60 g potassium hydroxide pellets added directly.

4) 100 ml pyridine plus 100 ml saturated aqueous potassium hydroxide.

5) 200 ml glycerol plus 60 g potassium hydroxide pellets added directly.

6) 200 ml saturated aqueous potassium hydroxide.

Each of these systems were added to a measured amount ($\cong$5 g) of crushed ($<$125 μ) quartz in a stainless-steel beaker, and heated to its boiling point at atmospheric pressure for a period of five hours. Quartz was chosen for these experiments because of its tight crystalline structure and relative insolubility in relation to other silica species (2). Solubility values for this mineral would represent a minimum for a given solvent system with respect to silica.

Solvent vapor was refluxed into each system by placing a volumetric flask of cold water over the mouth of the beaker. Undissolved quartz was trapped in base-resistant sharkskin filter paper and thoroughly washed with distilled water. The residue was then dried and weighed. Weight loss is expressed as percent of original weight (Table I).

TABLE I

Quartz

Solvent System	Temp. °C	Time (hr.)	Wt. loss*(%)
Quinoline + KOH pellets	235	5	55
Quinoline + Saturated Aqueous KOH	155	5	36

TABLE I (cont.)

Solvent System	Temp. °C	Time (hr.)	Wt. loss*(%)
Pyridine + KOH pellets	130	5	3
Pyridine + Saturated Aqueous KOH	115	5	7
Glycerol + KOH pellets	179	5	29
Saturated Aqueous KOH	110	5	9
	Oil Shale		
Quinoline + KOH pellets	235	5	37

*Figures are mean values for duplicate runs.

Problems were encountered in cleaning the undissolved quartz of gummy residue and precipitated potassium hydroxide which often formed as the solution cooled during filtering. In most cases, the residue was water soluble and was eliminated by repeated washing.

DISCUSSION

From the accumulated data (Table I) it can be seen that, of the solvent systems investigated, quinoline plus potassium-hydroxide pellets provided the best results, followed by a mixture of quinoline and aqueous saturated potassium hydroxide. Mixtures of pyridine and potassium hydroxide. Mixtures of pyridine and potassium hydroxide did not prove effective.

It is not clear why a basic quinoline system dissolves more quartz than a basic aqueous system, especially since potassium hydroxide is not readily soluble in quinoline. Attempts to dissolve potassium hydroxide in quinoline result in a dense milky suspension. This suspension may contain the active agent, perhaps a quaternary organic salt, that in water serves as a better hydroxyl source than solid potassium hydroxide. Practical grade quinoline was used for these experiments, and this may contain enough water to dissociate a quaternary salt.

A more probable explanation is that all the studied systems are undergoing aqueous potassium hydroxide reaction with quartz, and that the different degrees of solvent efficiency is merely a direct function of the temperature at which these reactions are occurring. Siever (3) has found that the solubility of silica in water increases with temperature, and it seems reasonable to assume that this general relationship is true for aqueous potassium hydroxide systems as well. All solvents used for these experiments, with the exception of pyridine, would be expected to contain small but perhaps significant amounts of water. There seems to be a general correlation between solvent capability and boiling point of the system (Fig. 1), suggesting that the organic solvents serve merely as a substrate to elevate the temperature of aqueous reactions.

A glycerol system was chosen to test this hypothesis, because its boiling point is considerably higher than that of other solvents used

in these experiments. It was found that glycerol and potassium hydroxide form a complex with a relatively low boiling point of 179°C, nonetheless the temperature and solvent capabilities of this system are in keeping with the proposed thesis. The pyridine system produced surprisingly poor results, but since reagent grade pyridine should have a negligible water content, the possibility of a good aqueous reaction is eliminated.

Addition of aqueous potassium hydroxide to the organic solvent would be expected to provide ample water for reaction, but would also decrease the boiling point of the system. The decrease in solvent efficiency of those systems that are aqueous by design might, then, be attributable to the decreased temperature of reaction. To support or disprove this hypothesis, additional experiments are planned to ascertain the solvent capability of each of the studied systems at the same temperature.

To test the practical applicability of the quinoline solvent system, a sample of raw crushed ($<125\ \mu$) Green River oil shale was extracted for five hourse with quinoline and potassium hydroxide pellets. The sample underwent a 37% weight loss, probably representing a large portion of the quartz and other silicates contained in the rock. X-ray analysis should provide an accurate evaluation of any mineralogic changes resulting from this extraction.

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REFERENCES

1. W. C. Meyer and T. F. Yen, The Effects of Bioleaching on Green River Oil Shale, This preprint, 1974.

2. R. K. Iler, The Colloid Chemistry of Silica and Silicates, Cornell Univ. Press, New York, p. 6, 1955.

3. R. Siever, Silica Solubility 0-200°C, and the Diagenesis of Silican Sediments, J. Geol., 70, 127-150 (1962).

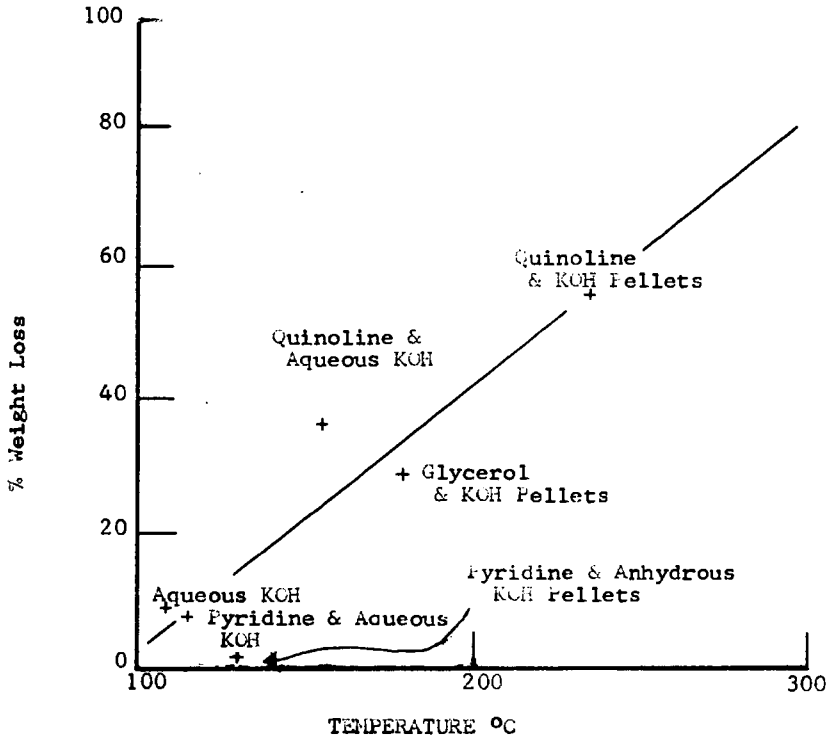

Fig. 1. Relationship of Solvent Capability to Temperature (Boiling Point of System).