color and composition than is possible with a brass anode. It also makes it possible to produce from the same bath a great variety of color and composition in brassing work.

THE CHEMISTRY OF ORE DEPOSITION—PRECIPITATION OF COPPER BY NATURAL SILICATES.[1]

By Eugene C. Sullivan.

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Work recently done in the chemical laboratory of the United States Geological Survey shows that natural silicates and especially feldspars enter into reactions of double decomposition with salt solutions at ordinary temperatures more readily than is generally recognized, and it appears possible that not only the importance of feldspars, estimated to make up 60 per cent. by weight of the lithosphere,[2] as precipitants in geological reactions, but also the great superiority of salt solutions over water as disintegrating agents, have not been sufficiently emphasized.

The work in question has suffered interruption for the present, and it is thought desirable to present in very brief outline, at this time, some of the results thus far obtained.

Lemberg[3] showed that sodium chloride solution at ordinary temperature transformed leucite ($KAlSi_2O_6$) partly into analcite ($NaAlSi_2O_6.H_2O$), sodium being substituted for the equivalent quantity of potassium. The reverse substitution took place when analcite was treated with potassium chloride solution.

The reaction

$$KAlSi_2O_6 + NaCl + H_2O \rightleftarrows NaAlSi_2O_6.H_2O + KCl$$

is similar to the familiar one

$$BaSO_4 + Na_2CO_3 \rightleftarrows BaCO_3 + Na_2SO_4.$$

Provided the mass law holds, equilibrium sets in when the concentrations of the substances have the following relation (formulas in brackets indicate concentrations):

$$[KAlSi_2O_6].[NaCl].[H_2O] = k[NaAlSi_2O_6.H_2O].[KCl],$$

k being the equilibrium constant. As the silicates are both present as solids, their active mass is constant, as is also that of the

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[1] Published by permission of the Director of the United States Geological Survey.

[2] F. W. Clarke: Bulletin U. S. Geol. Survey 228, p. 20.

[3] *Z. deutsch. geolog. Ges.*, **28**, 537 (1876).

water; substituting the concentrations of the ions concerned for those of the salts, we have $\frac{[Na^\cdot]}{[K^\cdot]} = \text{constant}$.

That is, equilibrium is attained when the concentrations of the sodium ion and the potassium ion are in a certain definite ratio. If $Na^\cdot$ is present in excess of this ratio solid analcite forms, withdrawing sodium from solution until the equilibrium ratio is established; if $K^\cdot$ is present in excess the reverse change takes place, again restoring the same equilibrium. Treating repeatedly with fresh portions of either salt would tend to convert the solid completely into the silicate containing the alkali used.

These considerations apply only in case both solids are allowed free contact with the solution. This might conceivably be prevented by the precipitation of a surface film on the particles of the original solids or by the formation of a layer of partly disintegrated material which the solution will not penetrate.

Way,[1] Eichhorn,[2] Peters, van Bemmelen,[3] and others obtained with soils, kaolin, etc., results precisely similar to those of Lemberg. The finely-divided solids take up base from a salt solution, giving off an equivalent quantity of their own constituents.

Following a suggestion made by Kohler,[4] the present writer first took up the action of kaolin on cupric sulphate solution.[5] Kohler discusses the possibility of a causal relation between the adsorptive capacity of clays and their association with the ores of certain metals, notably copper, adsorption referring to the power ascribed to solids, immersed in a solution, of concentrating the dissolved substances on their surface. Such action would be especially marked in the case of powdered or porous material.

A washed kaolin was used, containing 1.6 per cent. alkali, mostly potassium, and small quantities of calcium, magnesium and sulphates. Microscopic examination showed the presence of undecomposed feldspar.

Among other solids employed, all ground to a fine powder, were:

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[1] *Jour. Roy. Agr. Soc.*, **11**, 313 (1850); **13**, 123 (1852).

[2] Pogg. *Ann.*, **105**, 126 (1858).

[3] *Landw. Versuchsstationen*, **21**, 135 (1877); **23**, 264 (1879); **35**, 69 (1888); etc.

[4] Kohler: "Adsorptionsprozesse als Faktoren der Lagerstättenbildung und Lithogenesis." *Z. prakt. Geologie*, **11**, 49 (1903).

[5] The work with kaolin was undertaken at the suggestion of Mr. W. H. Weed, of the Geological Survey, in the hope of throwing light on the formation of Montana copper-ore deposits. The writer is much indebted to Mr. Weed for material and information on the geological side of the work.

Shale from Arizona, consisting largely of kaolin and glauconite and containing 6.74 per cent. K_2O and 0.44 per cent. Na_2O.[1]

Two specimens of orthoclase from San Diego County, California, fairly pure.[2]

Well-crystallized albite from Amelia Court House, Va.[3] Albite from this region is shown by analysis to be almost perfectly pure.

Crystalline microcline from Way's Quarry, near Wilmington, Delaware, also shown by analysis to be very pure.[2]

Pyrite, ground in water to a fine mud, washed with dilute sulphuric acid, water, alcohol, and ether, and dried at 100° C.

The kaolin, shale, and feldspars were subjected to quantitative tests for carbonate; none contained more than an insignificant trace.

To determine the action of a powdered solid on cupric sulphate solution, 25 grams of the powder were added to 50 cc. of the solution (in most cases a 1 per cent. solution of the crystalline $CuSO_4.5H_2O$, containing 0.252 gram copper in 100 cc.) in a flask which had been steamed to remove easily soluble matter from the glass. After being securely stoppered the mixture was allowed to stand for some time with occasional shaking and was then filtered. The perfectly clear filtrate was analyzed.

Some of the results are as follows: The reaction between the silicate and the copper solution is chiefly an exchange of bases, copper undergoing precipitation and an equivalent quantity of other bases (chiefly the alkali and alkaline earth bases) entering the solution. If adsorption takes place, it is in comparatively insignificant amount.

The acidity of the cupric sulphate solution is not changed by contact with the silicates and precipitation of copper. A certain quantity of SO_4 is precipitated with the copper—in several instances about $1SO_4 : 10Cu$. Whether the corresponding amount of cupric sulphate is adsorbed or whether some precipitation of basic sulphate takes place, as is the case when alkali is added to excess of cupric sulphate solution, remains to be determined. The sum of the bases which go into solution is exactly equivalent to the total copper precipitated, less the SO_4 precipitated.

The equilibrium actually attainable is decidedly dependent on

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[1] This shale was kindly furnished by Dr. Lindgren of the Geological Survey, who called the writer's attention to its frequent association with cuprite.

[2] Obtained through Mr. W. T. Schaller, of the U. S. Geological Survey.

[3] Kindly furnished by Mr. Wirt Tassin, of the U. S. National Museum.

the grinding; the finer the powder the more copper is precipitated. The action thus apparently takes place only on the surface of the particles.

The shale removed in one case 95 per cent., in another case the total copper from its solution. The solution remained perfectly neutral, K_2O, MgO, CaO, Na_2O and MnO replacing the copper.

The feldspars orthoclase, albite and microcline, ground in the agate mortar, each remove copper from solution to a surprising extent, 25 grams of the powdered solid taking from 60 to 100 mg. copper out of 50 cc. cupric sulphate solution containing 126 mg. copper. This is a greater precipitation than takes place with kaolin and also greater than that caused by an equal weight of pyrite. Results among different substances are, however, only roughly comparable, owing to the impossibility of getting the powders of the same degree of fineness. The feldspars, originally pure white, were given a decided green tinge by the precipitated copper. After a few washings, further treatment with water removed practically no copper at all from the greenish powder.

Cupric sulphate solution is similar to carbonic acid solution in the extent of its action on feldspar. Somewhat more material was dissolved from orthoclase by 1 per cent. cupric sulphate solution than by suspending in water and passing carbon dioxide for twenty hours. Water alone under similar conditions dissolved but a trace.

Work along the line of that described will be continued in this laboratory.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

ON AMORPHOUS SULPHUR: III. THE NATURE OF AMORPHOUS SULPHUR AND CONTRIBUTIONS TO THE STUDY OF THE INFLUENCE OF FOREIGN BODIES ON THE BEHAVIOR OF SUPERCOOLED MELTED SULPHUR.[1]

BY ALEXANDER SMITH AND WILLIS B. HOLMES.

Some Facts about Amorphous Sulphur Previously Established with More or Less Definiteness.—Insoluble or amorphous sulphur seems

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[1] A preliminary paper, including some of the present results, appeared in the *Ber.*, **35**, 2992 (1902). The experiments were all made before the work described in the