

were deposited by putting a small piece of zinc into a copper sulphate solution of 10~20% strength.

The X-ray analysis of specimens was performed by the Laue method, utilizing the heterogenous X-rays emitted from Cu and Fe anticathodes. The results thus obtained will be summarized as follows.

(1) When the distilled water was employed as solvent, it can be deduced in the Laue photograph that the metallic copper deposited from the 10% solution may be composed of perfectly irregular aggregation of the micro-crystals of the diameter  $10^{-3}$  cm~ $10^{-4}$  cm, but when the hard water was used as solvent, the copper from the same concentration as before, may be consisted of an irregular congregation of the micro-crystals of the diameter  $10^{-2}$  cm~ $10^{-3}$  cm accompanying with the aforesaid assemblage.

(2) The specimen which was deposited from the 20% solution, when the hard water was used as solvent, is made of two fibrous arrangements of the micro-crystals of appreciable size ( $10^{-3}$  cm in diameter), each having the axis of the indices  $\langle 110 \rangle$  in common. One of these fibrous arrangements has its common axis of the same indices coinciding with the parallel to the direction of growing, and the other has its common axis inclining with  $30^\circ$  to the direction of growing.

(3) Certain reddish-black colour materials which were deposited on the surface of zinc together with metallic copper, were determined as  $\text{Cu}_2\text{S}$  by means of the powder method.

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## 8. Quantitative Determination of Nickel and Cobalt in Sea Water

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Nickel in sea water has been studied by Ernst and Hörman (1936), and determined spectroscopically as 0.1  $\gamma$ /L. Cobalt has been detected in marine organisms and sea water, but not quantified yet.

The authors has colorimetrically quantified Ni and Co in sea water by the use of oxidized dimethylglyoximate method and thiocyanate method as follows;

Determination of Ni: 40-60L of sea water was taken and added 200 mg of Fe as  $\text{FeCl}_3$  solution. Then  $\text{Fe}(\text{OH})_3$  was precipitated with 60ml of  $\text{NH}_4\text{OH}$  (1 : 10), and allowed to stand for 2-3 days. The precipitate was filtered, and dissolved in 30ml of  $\text{HCl}$  (1 : 1), then added 10ml of 10% citrate solution and nearly neutrized, with  $\text{NH}_4\text{OH}$  just to alkaline. Then Ni was extracted 2 times with each 10ml of 1% dimethylglyoxime- $\text{CHCl}_3$  solution, and reextracted with 10ml of 5N- $\text{HCl}$  from  $\text{CHCl}_3$  layer. The  $\text{HCl}$  solution of Ni was treated with  $\text{Br}_2$  water, neutralized with

NH<sub>4</sub>OH to 2-3 drprs excess and then added 1 ml of 0.1% dimethylglyoxime alcohol solution. The solution was diluted to 25ml, and resultant color intensity of the solution was measured with pulfrich photometer. In this procedure, the recovery of Ni was found to be about 85%.

Determination of Co: 40-60L of sea water was taken and Co was coprecipitated with Fe (OH)<sub>3</sub>, and the precipitate was dissolved in HCl and made alkaline citrate solution as in the case of Ni. Then Co was extracted 3-times with each 5ml of 0.01% dithizone-CCl<sub>4</sub> solution. CCl<sub>4</sub> was evaporated to dryness, and ignited at the temperature less than 500°C. The residue was treated with a aquaregia and evaporated to nearly dryness. The residue was treated with a little water, and added 3ml of 10% NH<sub>4</sub>SCN solution, 3-4 drops of 20% SnCl<sub>2</sub> and 15ml of acetone, then diluted to 25ml. The resultant color intensity was measured. In this procedure, the recovery of Co was found to be about 80%.

The results: Ni and Co in the sea water off shore of Shirahama, Wakayama Prefecture, Japan was found to be 0.8γ Ni/L and 0.5γ Co/L.

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## 9. On Equilibrium Relation between C, Si in Pig Iron and Slag under One Atomospheric Pressure of Carbon Monoxide Gas

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In case of production of pig iron in blast furnace, the equilibrium relation between pig and slag is the most important factor. Therefore, we determined at 1400°C and 1500°C the equilibrium relation between C, Si in pig iron and SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> system slag under one atm. pressure of carbon monoxide gas. The carbon monoxide gas, which is produced by dropping formic acid into hot conc. sulphuric acid, is purified and is supplied to a hard porcelain tube. The sample, which was prepared from a high carbon white pig iron, artificial slag and metallic silicon is melted in a graphite crucible, which is placed in the above mentioned porcelain tube, and is kept under the planned various lengths of time under one atm. at 1400°C and 1500°C.

Now the graphite crucible is taken out from porcelain tube, and is cooled in water as soon as possible. Temperature is measured by both the optical pyrometer and Pt-PtRh pyrometer.

We determined firstly the duration of time which pig and slag reached the equilibrium. Then we determined the equilibrium relation between the pig and