Kinetics of the Reduction of Selenious Acid by Sulfur Dioxide. III. Application to Recovery and Purification of Selenium in Sulfuric Acid Works

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The greater part of the starting materials for the productions of selenium consists of an anode-slime deposited in the electrolytic refining of copper and a sludge containing selenium recovered in the manufacturing process of sulfuric acid. The latter is called sulfuric acid sludge.

The reaction of selenious acid by sulfur dioxide was found to be a reversible reaction in sulfuric acid. The general equation for the rate constant of the forward reaction and the relation between the rate constant and the maximum percentage completion (maximum yield) were derived in the previous paper[1].

A great deal of sludge has recently been recovered from the mist acid which is a by-product of the manufacture of sulfuric acid, and a very simple and economical method of purification of selenium has been found by means of the application of the experimental results[1].

Application to the Recovery of Selenium in the Mist Acid.—A schematic diagram of the contact process for manufacturing sulfuric acid is shown in Fig. 1. Generally pyrites have about 12.6 parts of selenium per million[2] of pyrites. When pyrite is roasted, the selenium in the

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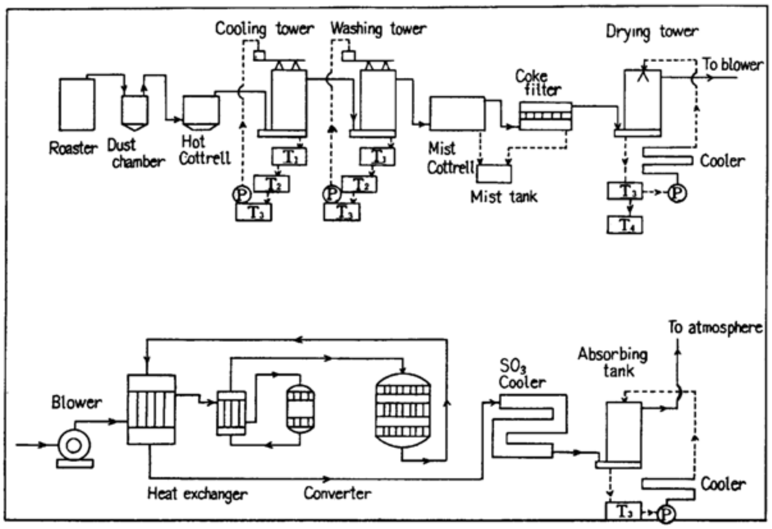

Fig. 1. Schematic diagram of contact process of sulfuric acid.

T_1: Cooling tank
T_2: Precipitating tank
T_3: Pump tank
T_4: Storage tank
Ⓟ: Pump
→— Gas
→-- Acid

pyrite is oxidized to selenium dioxide. The part of the selenium dioxide is dissolved in the mist acid*, which is excluded from gas by a mist Cottrell and a coke filter, and is brought into a mist tank. The concentration of the mist acid is about 15° Bé (s. g. 1.115) while the acid is saturated with sulfur dioxide. Nevertheless, a large quantity of selenious acid exists in mist acid without being reduced to selenium. This fact can easily by explained according to the results of Part II[1] of this series, as follows. The reaction of selenious acid with sulfur dioxide in sulfuric acid is reversible, and the rate constant of the forward reaction, k_2, is expressed according to the following equation:

$$k_2=2.054\times 10^{15}\times [\mathrm{H}^+]^2\times \exp\,(-E/\boldsymbol{R}T) \qquad (E=22.5\ \text{kcal./mol.}) \tag{1}$$

The equation which expresses the relation among rate constant, k_2, maximum percentage completion, x_m, and initial concentration of selenious acid, a, is as follows:

$$x_\mathrm{m}=1.306\times (k_2\cdot a)^{0.114} \tag{2}$$

In these equations, $[\mathrm{H}^+]$ is hydrogen ion concentration, T absolute temperature of solution, E the energy of activation, $\boldsymbol{R}$ the gas constant and a initial concentration of selenious acid. It is evident that maximum yield, x_m, depends heavily on temperature at the constant $[\mathrm{H}^+]$ and a, according to Eqs. 1 and 2. When the mist acid is heated up to the boiling point, selenium can be precipitated. After heating the mist acid, the selenium content in the mist acid is found to be about 0.00015 mol./l. Ninety-five per cent of selenium in the mist acid can be recovered by only heating the mist acid. Selenium sludge gained from the mist acid has a high content of selenium (about 80%), and a great deal of sludge can be recovered each day, making sludge a useful and plentiful starting substance for the isolation of selenium.

Application to the Purification of Selenium.—Up to the present time, many studies[3-33]

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* The mist acid has about 0.003 mol. selenious acid per liter.

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have been performed concerning the purification of selenium, and each method of purification of selenium has had its own characteristics.

In the purification of sulfuric acid sludge, the Stahl[8] and Littmann[9] method was found to be the most suitable. However, the method has some difficulty, the yield is relatively lower (around 85%). The present author has noticed that the yield depended largely on the hydrogen ion concentration and temperature according to Eqs. 1 and 2. Therefore, these two factors were taken into account for their method[8,9] as described subsequently.

Experimental

A great success has been attained in the purification of selenium on the industrial scale by enlarging the experimental procedures. Therefore, the process on an industrial scale will now be described in some detail. Figure 2 shows the schematic diagram of the plant for purification of sulfuric acid sludge according to the new method.

The dried sludge is brought into a reacting vessel, and 20 l. of fuming sulfuric acid (23%) per 1 kg. pure selenium in the sludge is added to the vessel.

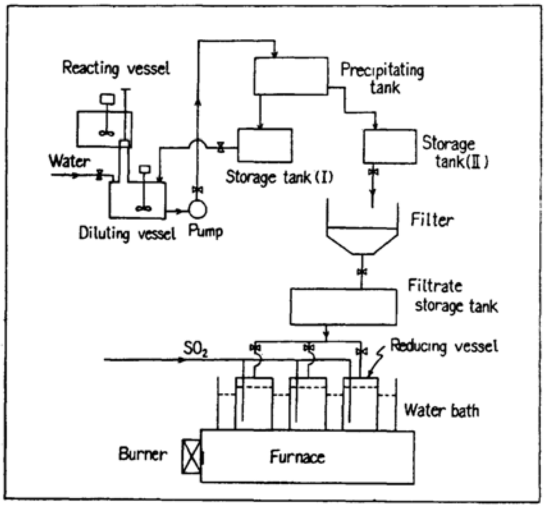

Fig. 2. Schematic diagram of purification plant of selenium.

These mixtures are agitated for two hours with a stirrer. The selenium in the sludge is changed to green selenium anhydro-sulphate ($SeSO_3$) according to the following reaction:

$$Se + H_2SO_4 \cdot SO_3 = SeSO_3 + H_2SO_4$$

Then, 2 l. of nitric acid (62% by weight) per 1 kg. pure selenium in the sludge is added to this green solution, and agitation is continued for one additional hour.

The temperature is increased up to about 120°C, and a yellow solution of selenious acid results as follows.

$$SeSO_3 + 4HNO_3 = H_2SeO_3 + H_2SO_4 + 4NO_2$$

The mixture containing selenious acid is slowly dropped into a diluting vessel, to which 50 l. of water per 1 kg. pure selenium in the sludge has previously been added. The temperature of the solution is elevated up to approximately 140°C, by the heat of the dilution of the fuming sulfuric acid. The excess of nitric acid is released owing to the high temperature. Moreover, 20 l. of water per 1 kg. pure selenium is added to the above solution.

The mixtures in the diluting vessel are pumped up to a precipitating tank, and cooled to the chamber temperature. Solid materials in solution, of course, settle down in this tank. The supernatant is brought into a storage tank (I), and subsequently sent to a filter. The filtrate is introduced into reducing vessels via a filtrate storage tank, and reduced to selenium by some previously water-washed sulfur dioxide (about 6%) used in the manufacture of sulfuric acid. When the solution of selenious acid is reduced, it is kept at bout 70°C[*1] in a water bath.

The selenium precipitated in the reducing vessel is removed, washed by water till all traces of sulfuric acid disappear and dried in an air bath at 110°C or lower. The waste solution is 35% (by weight) sulfuric acid, and this solution can be utilized elsewhere in industry.

Results

The purpose of the present study is to find the most suitable method for manufacture of selenium that meets the minimum commercial requirements in the sulfuric acid works.

A 92% yield[*2] has been secured and the purity of 99.9% has been obtained according to this new method. Table I shows a few

TABLE I. DATA OF ANALYSIS OF PURIFIED Se AND RAW MATERIALS

	Se, %	Fe	Si	Te	Hg	As	Ag	Pb
Purified Se (A)	99.94	w	w	www	s	nil	ww	nil
Raw material (A)	29.63	ss	s	s	s	ww	s	ss
Purified Se (B)	99.97	w	w	www	w	nil	ww	nil
Raw material (B)	88.99	ss	s	s	w	ww	s	ss

w, weak; ww, very weak; www, trace; s, strong; ss, very strong.

[*1] It is evident according to Eqs. 1 and 2[1] that the higher the temperature of the solution is, the greater the yield is. However, the particles of selenium separated at high temperature (about 80°C) are very small. At about 70°C, most particles of the precipitated selenium can pass through a 80~100 mesh sieve, and so they meet commercial requirements. The difference of yield between those at 70°C and at 80°C can hardly be appreciated by the present experiments.

[*2] Yield of conventional methods is between 80 and 90%.

examples of analysis*3 of selenium purified by the new method and raw materials.

Table I expresses the relative strength of the lines of emission spectra, except the data for selenium. A remarkable result is shown in Table I, namely, tellurium can be removed without any special effort, but on the contrary, most of the mercury remains in the purified selenium.

Discussion

Selenium in mist acid can be recovered by heating the acid according to the results of Part II[1] of this series.

By improving the Stahl[8] and Littman[9] method according to the results of Part II[1], the simple method for purification of selenium has been found. It was already mentioned in the present paper that this method had many virtues. Especially, it is interesting to note that tellurium can be excluded from the purified selenium without any special steps. According to conventional methods, some special steps were necessary in order to exclude impurities; for example, tellurium. These special processes are: i) using hydrochloric acid[10], ii) ion-exchange resin[34], and iii) distillation[11,15,33,35-39,42]. But it is unnecessary to include any provisions for removal of tellurium in the present method*4,[40,41].

It is the defect of this method that the purity of four nine can not be secured, although that of three nine can be secured. This seems to be caused by the mercury as an impurity.

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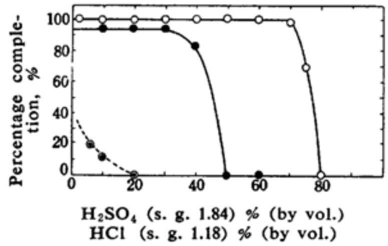

Fig. 3. Reduction of tellurous acid by SO_2.
◉ In acidic soln. with H_2SO_4
● In acidic soln. with {H_2SO_4+10cc. HCl(s. g. 1.18)}
○ In acidic soln. with HCl

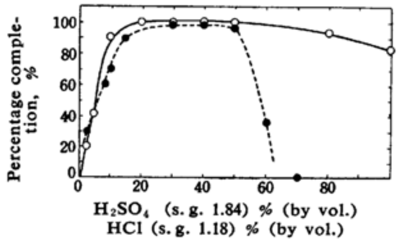

Fig. 4. Reduction of selenious acid by SO_2.
○ In acidic soln. with H_2SO_4
● In acidic soln. with HCl

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*3 Selenium is determined by means of gravimetric analysis, while others were determined by spectrochemical analysis.

*4 It is believed that, tellurium is excluded based on this fact, the higher the concentration of sulfuric acid, the smaller is the rate constant of reduction of tellurous acid in sulfuric acid. This can be guessed by the following simple, qualitative experiment. A solution of tellurous acid of 0.01 mol. per 200 ml. sulfuric acid of many kinds of concentrations were prepared, and left overnight at chamber temperature after being saturated with sulfur dioxide. Fig. 3 shows the plot of the tellurium precipitated (percentage completion) against each concentration of sulfuric acid. One can see that when the concentration of sulfuric acid is above 20% (by volume), tellurium can not be precipitated. Fig. 4 is the same plot as in the case of selenious acid for comparison with Fig. 3.

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