WATANABE LABORATORY.

(Director: Prof. Dr. Toshio Watanabe.)

A) Recovery of Tin from Tin Ores by Selective Reduction Followed by Leaching of Copper Salt Solution.

By **Toshio Watanabe** and **Tomosuke Nomitsu.**

I. Ordinary Smelting Process of Tin Ores and its Defect.

The tin ores are usually cassiterite SnO_2. Only the pure rich ores may be reduced directly to crude tin in a shaft furnace. Most of the lode tin is poor, containing often 1% Sn or even less, and is associated with many undesirable minerals, such as arsenopyrite, copper pyrite, iron pyrite, etc. Such poor ores must first be concentrated by the dressing processes taking advantages of the high specific gravity of the cassiterite. Gravity concentration is often combined with flotation, roasting or some chemical treatment to remove as many of the impurites as possible. By these means, the tin contents of the ore are raised to 50% or more. The concentrate thus prepared is reduced to crude tin in the reverberatory furnace, and is usually refined by liquation and tossing. The crude tin obtained from the Akenobe Mine, Hyôgo Prefecture, Japan, contains a considerable quantity of Cu, Fe etc., in spite of the use of the flotation and is refined electrolytically at the Mitsubishi Osaka Refinery.

The high concentration ratio in the dressing practice of the tin ores causes heavy loss of tin amounting to 30% or more during dressing. This loss may be reduced, if the grade of the concentrate is lowered, but a low grade concentrate produces a large quantity of slag in the next smelting in the reverberatory furnace which increases the loss of tin carried in the slag. Therefore that the ordinary dry process is suitable for smelting pure and rich ores, but not for smelting impure and poor ores. Studying the metallurgical process for the low grade impure tin ores, the authors devised a new method, which is explained below.

II. Outline of the New Method.

The concentrate which contains about 25% of tin, should be roasted by the selective reducing roasting process; thus the cassiterite is reduced to metallic tin, while iron oxides which are associated usually in large quantity in the ores, are kept in the state of FeO or Fe_3O_4. When the equilibrium diagrams (Figs. 1 & 2) of the reducing reactions of iron oxides and tin oxide are taken into

consideration, this procedure can be done easily : i.e. by maintaining the reducing temperature at 700°~900°C, and by regulating the contents of of CO and H_2 in the reducing gas. The figures 1 and 2 are made from the data given by Matsubara[1], Eastman[2][3], Robinson[3] and Maeda[4].
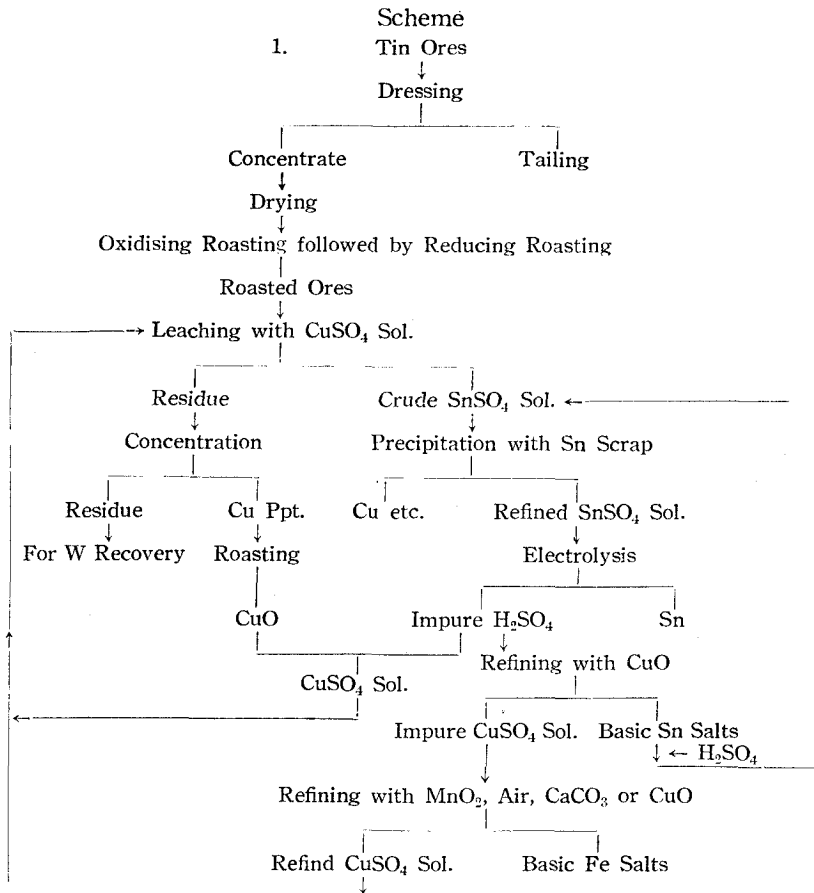
Fig. 1.

Fig. 2.
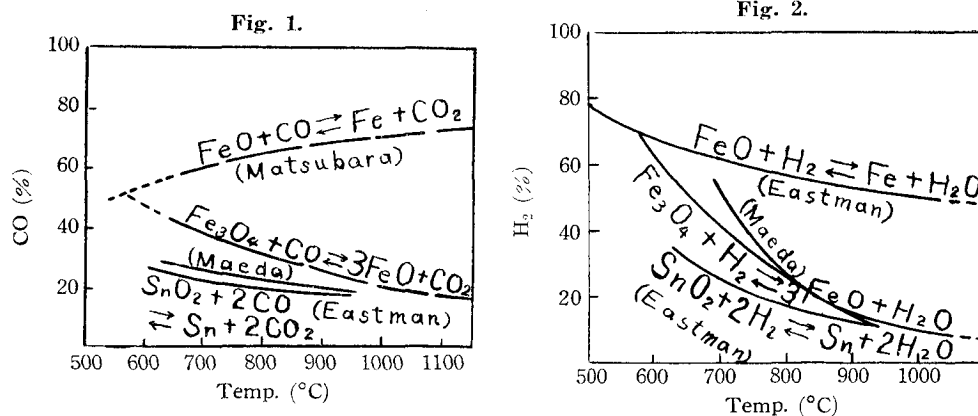
Even though the composition of the reducing gas is such as to reduce both iron and tin into metals at the temperature in a furnace, the selective reduction can be made by introducing the air into the gas, or by regulating the velocity of the flowing gas and properly increasing CO_2 and H_2O which are the reduction products in the furnace. In determining the percentage of the quantity of tin contained in concentrate, the economical standpoint should be taken into account. When the ores which have passed through reducing roasting are leached by copper sulphate or copper chloride solution, the copper is separated as the precipitate, and tin sulphate or tin chloride solution is obtained. From the tin sulphate solution, tin is precipitated by electrolysis; to the tin chloride solution is added limestone powder, which precipitates tin as tin hydroxide and basic tin salts. The precipitates thus obtained become metallic tin through reduction after calcination. Tin sulphate solution is a better solution for electrolysis, than chloride in current efficiency, and, moreover, is little affected by iron.

By making the sulphuric acid regenerated by electrolysis react on copper oxide gained by roasting the precipitated copper, a copper sulphate solution is produced and used for repeated leaching. When it is repeatedly used, iron and other materials gradually become accumulated in the solution. Therefore it is necessary to refine the solution. The method of its refinement is to separate and recover the tin remaining in the solution as basic tin salts by adding

1) Matsubara : Trans. Am. Inst. Min. & Met. Eng., 67, (1922) p. 13.
2) Eastman : Journ. Americ. Chem. Soc., 46, (1824), p. 888.
3) Eastman & Robinson : Journ. Americ. Chem. Soc., 50, (1928), p. 1106.
4) Maeda : Bulletin of the Inst. of Phy. & Chem. Research. Tokyo.

excessive copper oxide to a part of the spent solution after electrolysis; and then to make bivalent tin trivalent by carbon dioxide and the air, and again to precipitate iron and other materials with the addition of copper oxide or lime-stone powder. Copper chloride solution is regenerated by the following method: by adding pyrite to the precipitated copper, roasting it, and leaching with water and dilute sulphuric acid, a copper sulphate solution is produced; by adding to the copper sulphate solution calcium chloride, which is obtainable when tin is precipitated by adding limestone powder to tin chloride solution, copper chloride solution is produced. Some tin ores contain wolframite, which is difficult to separate completely by magnetic separation. But the above-mentioned procedure being followed, its magnetism is increased by reducing roasting; and without undergoing any action of copper sulphate solution or copper chloride solution, it remains with gangue in the residue and so it can be separated by gravity concentration or by magnetic separation.

Scheme

1. Tin Ores
        ↓
    Dressing
        |
    ┌───────────────────┴───────────────┐
Concentrate   Tailing
    ↓
Drying
    ↓
Oxidising Roasting followed by Reducing Roasting
    |
Roasted Ores
    ↓
Leaching with $CuSO_4$ Sol.
    |
┌───────────────┴───────────────────────┐
Residue   Crude $SnSO_4$ Sol. ←
    ↓   ↓
Concentration   Precipitation with Sn Scrap
    | |
┌───────┴───────┐   ┌────────────┴────────────┐
Residue   Cu Ppt.   Cu etc.   Refined $SnSO_4$ Sol.
    ↓   ↓   ↓
For W Recovery Roasting   Electrolysis
                | |
              CuO   ┌───────────────┴───────┐
                | Impure H_2SO_4 Sn
        ┌───────┴───────┐   ↓
    $CuSO_4$ Sol.   Refining with CuO
                                    |
                        ┌───────────┴───────────┐
            Impure $CuSO_4$ Sol.   Basic Sn Salts
                        | ↓ ← H_2SO_4
            Refining with MnO_2, Air, $CaCO_3$ or CuO
                        |
            ┌───────────┴───────────┐
   Refind $CuSO_4$ Sol.   Basic Fe Salts
            ↓

When tin ores contain much copper they should be at first, even according to the new method, be separated and recovered by flotation. But when they contain a small quantity of copper, the existece of copper has little influence on the extraction % of tin, through they are subjected to the new process directly.

When both tin and iron are reduced to metals without selective reduction, an alloy is produced, which makes the solubility of tin more difficult in the next leaching.

III. Schemes of the New Process and Examples of the Kg Test.

A brief outline of the new method has been given above; and the scheme of the new method is as follows:
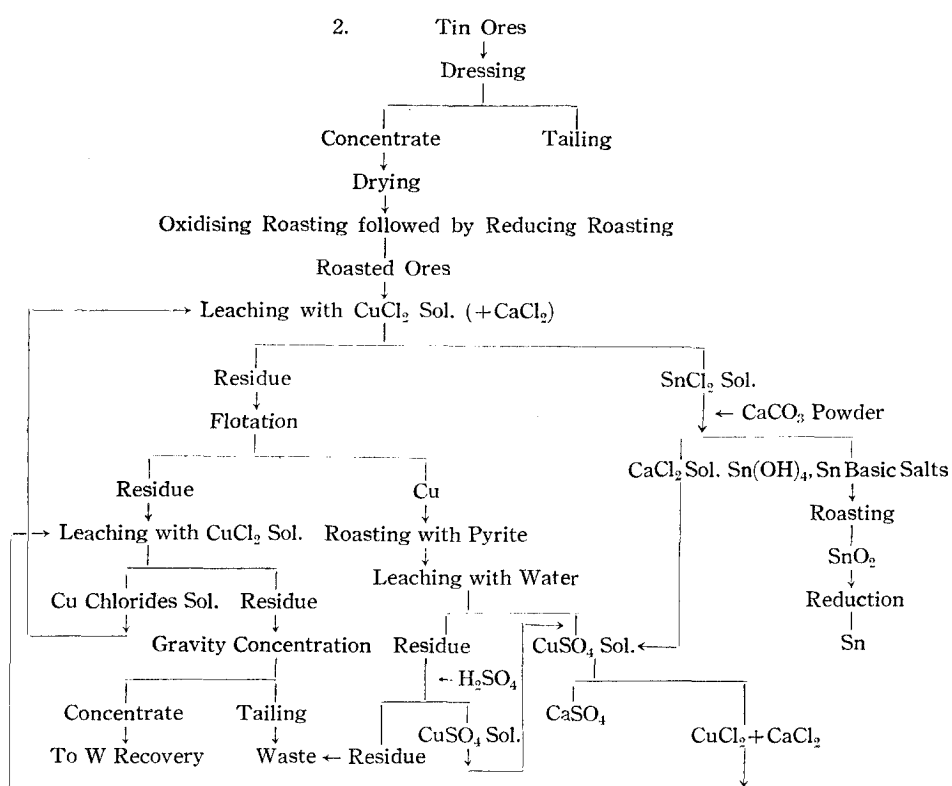
The authors studied such subjects as reducing, roasting and leaching, of the ores electrolysis and refining of tin solutions. The details of those studies have been reported in "The Saiko-Yakin Geppo" Vol. 11, No. 4, 5, 7, 9, 10, 11 (1933), Vol. 12, No. 4 (1934), Vol. 13, No. 11, 12 (1935). The following is one of the results obtained by the Kg. Test;

An example of the Kg Test (sample 3.0 Kg).

The analysis of the ore (%): Sn 23.5, Fe 7.6, Cu 0.1.

The roasting temperature: about 800°C.

The composition of the reducing gas (%):

CO_2 2.2, O_2 7.1, CuH_2u 2.4, CO 7.8, CH_4 21.0, H_2 28.1, N_2 31.4.

The reducing percentage of tin: 93.8%, the solubility of tin (copper chloride solution): 97.7% (for the reduced tin).

The solubility of tin from the ores $93.8 \times 97.7 = 91.6\%$.

The precipitating percentage by limestone power: 99.6%.

The reducing percentage of the precipitate, which was produced by limestone, by charcoal (tin obtained in a lump): about 83%. Tin powder adhering on the walls and on the surface of the lump of tin, may be recovered by dissolving in copper chloride solution.

When a great quantity of sample is used, the rate of the production of lump tin is great, compared with when a small quantity is used.

B) A New Metallurgical Process of Tungsten Ores.

By **Toshio Watanabe** and **Tomosuke Nomitsu.**

I. General.

1. Ordinary Metallurgical Process of Tungsten Ores.

Ferro-tungsten is usually obtainable from tungsten ores by reducing tungsten concentrate with a proper quantity of a reducing agent and flux at high temperatures in an electric furnace. The Thermit process is sometimes applied as well.

The ordinary method of obtaining the metallic W from tungsten ores is as follows: W is obtained by reducing WO_3, which has been produced as pure as possible by some chemical process, with carbon or hydrogen. WO_3 is produced thus: an infusion is first made by leaching the tungsten concentrate with sodium carbonate sintered by heating; and it is turned into WO_3 by acid. Another method is to make a sodium tungstate solution by leaching the concentrate with caustic alkaline solution.

2. An Outline of the New Process.

The new process the authors have devised at the Institute for Chemical Research of the Kyoto Imperial University is as follows; to wolframite ores containing about 5—20% of W is added a chloride or sulphate of an alkaline metal, or to a low grade scheelite concentrate is added a chloride of an alkaline metal. By heating it to about 700°—900°C and passing steam vapour over it, W is turned into tungstate of alkaline metal, which is leached with water. To this solution is added calcium chloride solution to precipitate W as calcium tungstate. This tungstate is decomposed into WO_3 with hydrochloric

acid, which being reduced with carbon, becomes the metal W. The metal W is pressed with spongy iron, and thus cake is obtained, which, after melting at high temperatures in the electric furnace easily becomes ferro-tungsten.

When wolframite ores contain a small quantity of Mn, it is unnecessary for the new process to pass the steam; and passing only air or other gases makes the majority of W soluble in water. When, on the contrary, wolframite ores contain a considerably large quantity of Mn, it is difficult to make W soluble in water without passing the steam. Besides, the above mentioned reaction is seldom produced by heating only in a closed vessel, adding NaCl or Na_2SO_4.

According to this new process, the treatment of low grade concentrate is, as shown above, made possible, and at the same time the separation of W from cassiterite is facilitated, because though the ores contain cassiterite, neither cassiterite nor anhydrous silica, as seen in many examples, becomes soluble in water.

3. Comparison of the New Process with the Ordinary Process.

Using the ordinary method of bringing W into aqueous solution after treating tungsten concentrate with sodium carbonate or caustic alkali, both silica and cassiterite enter the solution, and so these impurities must be preliminarily removed as completely as possible by dressing. Again, in the ordinary process fully dressed concentrate is used to make ferro-tungsten, while wolframite is apt to become a fine powder in the course of crushing, and so a good recovery by gravity concentration cannot be expected. Cassiterite and wolframite are difficult to separate by gravity concentration; though wolframite bears a slight magnetism, the magnetic separation of both is not so effectual.

According to the new process, however, there is little need of dressing, and even about 90—95% of W contained in low grade concentrate may be taken out as the metallic W or ferro-tungsten. Accordingly the total recovery by dressing and metallurgical treatments can be increased much more than by the ordinary process. The new process, when applied to the ore containing both cassiterate and tungsten minerals, is advantageous as well. Further, as far as the price of flux is concerned, salt to be used in the new method is far cheaper than carbonate soda in the ordinary method.

II. The Experiments of Roasting and Leaching.

1. The Influence of Steam Vapour.

Adding salt or sodium sulphate to each of such samples as ferberite, hübnerite (artificial) and wolframite, (each containing about 10% of WO_3), passing steam or air while heating, and then leaching with water, the solubility of WO_3 was measured, and the results thus obtained are given in Figs. 1, 2 and 3.
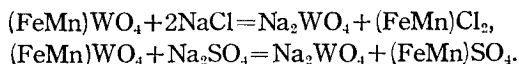
The conditions of the experiments.

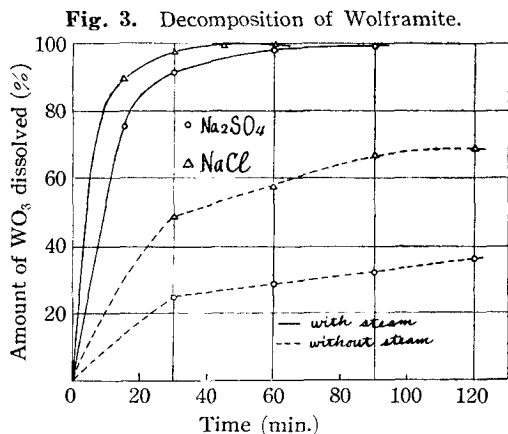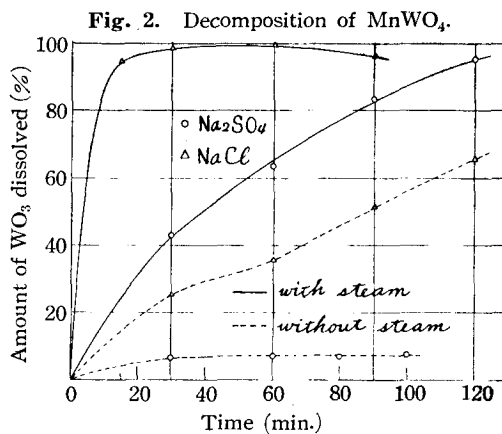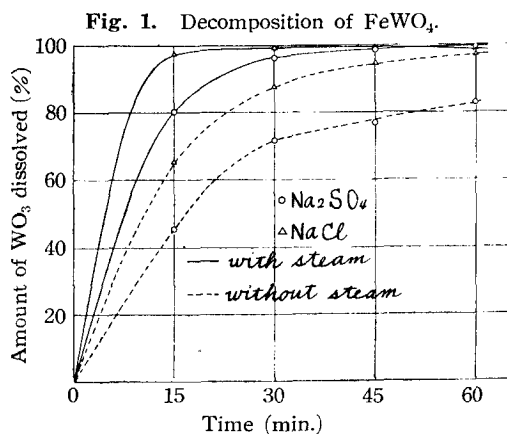The roasting temperature: 740°—760°C. when NaCl is used.

    820°—840°C. when Na_2SO_4 is used.

The quantities of NaCl and Na_2SO_4: three times as much as those obtained

from the following equations:

$$(FeMn)WO_4 + 2NaCl = Na_2WO_4 + (FeMn)Cl_2,$$
$$(FeMn)WO_4 + Na_2SO_4 = Na_2WO_4 + (FeMn)SO_4.$$

The size of the ore-grain: smaller than 100 meshes.

Fig. 1. Decomposition of FeWO₄.

Fig. 2. Decomposition of MnWO₄.

Fig. 3. Decomposition of Wolframite.

It is seen that W becomes more soluble in water by heating and passing vapour over it.

2. The Influence of the Quantity of Air.

Adding salt to various kinds of tungsten samples, passing air while heating, a number of experiments were carried out with the variation of the quantity of air. The result obtained is shown in Fig. 4. The roasting temperature and the quantity of salt are the same as those in the previous experiments.

The time of roasting: 30 minutes.

It is admitted from Fig. 4 that WO₃ in the tungsten ores cannot be changed into soluble compound in water only by heating with salt in a closed vessel; when salt is added and air is passed over it while heating, the majority of W

in ferberite becomes soluble in water; while other kinds of tungsten ores do not become soluble in water so easily as W in ferberite.

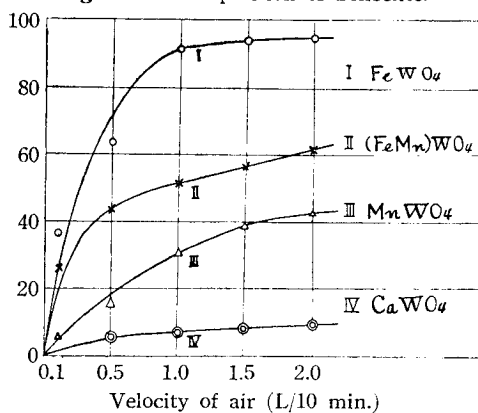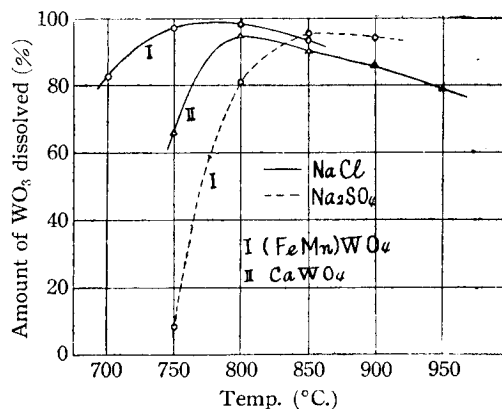Fig. 4. Decomposition of Scheelite.

Fig. 5. Influence of Temp. on Decomposition of Wolframite and Scheelite.

Fig. 4. Decomposition of Scheelite.

Fig. 5. Influence of Temp. on Decomposition of Wolframite and Scheelite.

3. The Influence of the Roasting Temperature.

Salt or sodium sulphate was added to a mixture of wolframite and SiO_2, to which steam was passed while heating. Thus the influence of the roasting temperature was examined, the results of which are shown in Fig. 5.

Fig. 5 shows that proper roasting temperatures are about 750°-800°C. when NaCl is used, and about 850°C. when Na_2SO_4 is used.

4. The Behavior of Anhydrous Silica or Cassiterate in the New Process.

By adding salt or sodium sulphate to anhydrous silica and passing steam while heating, a small quantity of SiO_2 may become soluble in water, but, the quantity is so small it may be said that silica does not turn, in practice, soluble in water.
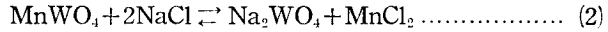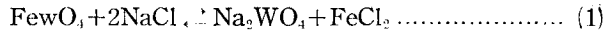
Adding salt or sodium sulphate to cassiterite and passing steam or air while heating to about 900°C. does not cause tin to become soluble in water.

5. Consideration of the Reaction that is the Basis of the New Process.

$MnWO_4$ is obtained by adding salt or manganese chloride to Na_2WO_4 and fusing at about 800°C. When manganese chloride is substituted by ferrous chloride, $FeWO_4$ is obtained. These processes have long been used as the dry process of manufacturing $MnWO_4$ or $FeWO_4$.

According to the new process using NaCl or Na_2SO_4, Na_2WO_4 which is soluble in water, is obtained from $FeWO_4$, $MnWO_4$, etc. This reaction is the reverse at that used in the ordinary method of manufacturing $FeWO_4$, $MnWO_4$, etc. That is, reactions (1) and (2) are reversible at high temperatures; they may be led in either direction, right or left according to the conditions causing them. It may be considered that when made to react on steam or air, (1) and (2) proceed to the right, $FeCl_2$ and $MnCl_2$, etc. produced by the reactions being quickly decomposed and vanish.

$$FewO_4 + 2NaCl \rightleftarrows Na_2WO_4 + FeCl_2 \ \dots\dots\dots\dots\dots\dots\dots \ (1)$$
$$MnWO_4 + 2NaCl \rightleftarrows Na_2WO_4 + MnCl_2 \ \dots\dots\dots\dots\dots \ (2)$$

III. Manufacturing of the Metallic W, or Ferro Tungsten from the Solution.
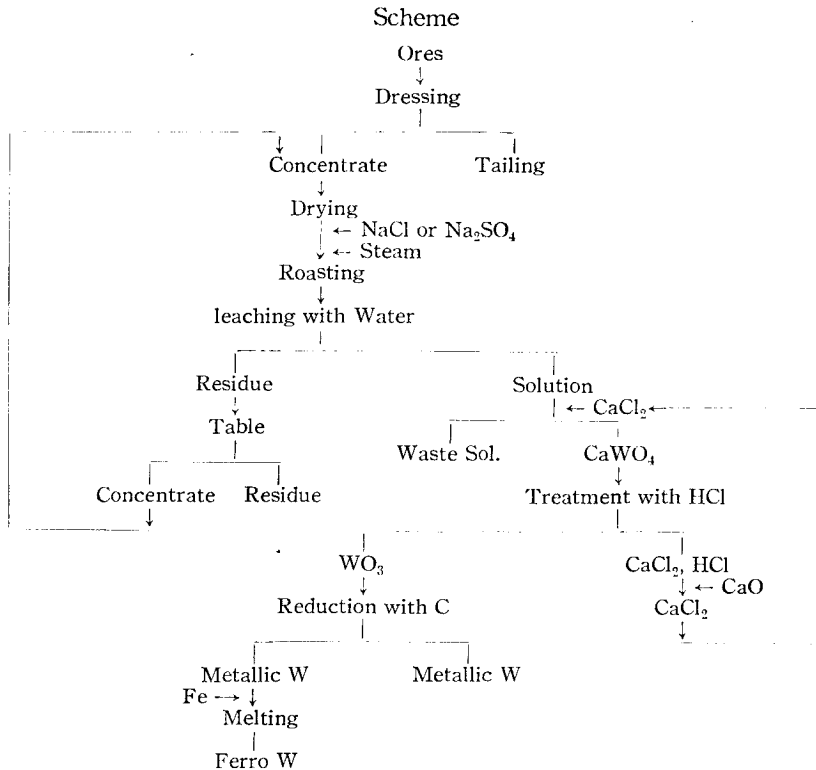
The manufacture of WO_3 from sodium tungstate solution has been the subject of much study. The authors obtained WO_3 by the following process: W was precipitated as $CaWO_4$, adding solution to the infusion, and it was decomposed with HCl to turn to WO_3.

As to the reduction of WO_3, the metal containing a small quantity of carbon was obtained, using, according to Mennicke's work, powdered carbon and rosin for the reducing agents.

Ferro tungsten could be easily prepared from the metal W by mixing powdered W and spongy iron in a given proportion and melting at high temperatures in the electric arc furnace.

IV. Conclusion.

The scheme of the new metallurgical process of tungsten ores is as follows:

Scheme

```
                            Ores
                             ↓
                          Dressing
                             |
              ┌──────────────┴──────────┐
              ↓                          |
         Concentrate                 Tailing
              ↓
          Drying
              | ← NaCl or Na₂SO₄
              ↓ ← Steam
          Roasting
              ↓
       leaching with Water
              |
        ┌─────┴──────────────────┐
     Residue                  Solution
        ↓                        | ← CaCl₂ ←
      Table               ┌──────┴──────┐
        |              Waste Sol.     CaWO₄
   ┌────┴────┐                          ↓
Concentrate Residue            Treatment with HCl
     ↓                                  |
                                   ┌────┴────┐
            WO₃                 CaCl₂, HCl
             ↓                         ↓ ← CaO
      Reduction with C             CaCl₂
             |                         ↓
      ┌──────┴──────┐
  Metallic W    Metallic W
Fe → ↓
   Melting
      |
   Ferro W
```

$$FewO_4 + 2NaCl \rightleftarrows Na_2WO_4 + FeCl_2$$

As said in the general remarks, the new process does not requires so high grade a concentrate as does the ordinary process. Low grade concentrate can be used directly. It follows, therefore, that much of the loss by dressing may be saved in this process.

W has easily been separated from cassiterite in ores containing cassiterite without any preliminary separation by dressing, and hence the metal W or ferro tungsten containing no tin has been obtained.

Further, in the present method sodium carbonate used in the ordinary method may be substituted by cheaper salt or sodium sulphate.