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## 論 文 内 容 要 旨

Metallurgical industry is one of the largest energy consumers. The total energy consumption for metal production is near 12% of the total energy consumption of the world. Over the past 20 years, many energy-saving processes have been developed, but the energy conservation is still a hard task for metallurgists.

The application of organic solvents in hydrometallurgy is a important development. Besides solvent extraction, the application of water-soluble solvents to hydrometallurgy is a new metallurgy area. As an evidence, alcohol crystallization method is an attractive process for its less energy consumption.

Alcohols are widely used in industry. They are characterized by the presence of hydroxyl group (s). Because the molecular structures of alcohols are much different from that of water, the large changes are observed in solubility, complexation, redox potentials, equilibria, etc. These special properties offer great opportunity for developing untraditional metallurgical processes. The following 5 subjects are from 5 angles to treat the relationships among salts, water and alcohols.

### 1. NITRATE PROMOTED LEACH AND ALCOHOL CRYSTALLIZATION FOR TREATING NICKEL-BEARING PYRRHOTITE

Nikel-copper ores usually contain abundant pyrrhotite. For increasing the production efficien-

cy of smelters, the common practice is to raise concentrate grade by ore dressing. Thus a large amount of nickel-bearing pyrrhotite is now discarded as middling. It presents a significant loss of nickel resources. A great deal of researches has been done to develop practical methods for the treatment of nickel-bearing pyrrhotite, however, only a few are in commercial use.

Nitric acid is a strong oxidant. In leaching process, nitrogen monoxide can be oxidized by oxygen into nitrogen dioxide, which dissolves in water and forms nitric acid again. Thus, nitrogen monoxide acts as an oxygen-carrier which conveys oxygen from gas phase into solution to accelerate leach reactions. That is so called nitric acid promoted leach.

The composition of a typical nickel-bearing pyrrhotite concentrate treated is 2.5% Ni, 1.6% Cu, 0.1% Co, 30.1% Fe, 15.1% S and 18.2% MgO. A large amount of magnesium compounds exists in the concentrate. It was treated by nitric acid promoted leach under the following conditions:  $\text{HNO}_3$  5%, L:S=4:1,  $\text{Po}_2$  4.5kg/cm<sup>2</sup>, 100°C, the leaching efficiency of Ni reached 92%, correspondingly, Cu 94%, Co 75.1%. During nitric acid leach, almost all the magnesium compounds dissolved into solution as magnesium nitrate and sulfate, which consumed a large amount of nitric acid and sulfuric acid. Therefore, how to regenerate nitric acid to reduce the consumption of nitric acid and how to separate magnesium sulfate to avoid its accumulation becomes the key of this process.

In order to get a clear understanding of the solubilities of magnesium sulfate and magnesium nitrate in their mixed solution, the equilibrium phase diagrams of  $\text{Mg}(\text{NO}_3)_2$ - $\text{MgSO}_4$ - $\text{H}_2\text{O}$  system at 25, 35 and 70°C have been determined. From them, the energy consumption for removing magnesium chloride can be estimated. The results indicated that the separations of  $\text{MgSO}_4$  both by evaporation and by alcohol crystallization are effective. But the heat consumptions for removing one gram of  $\text{MgSO}_4$  are much different: the heat consumption by adding alcohol to 10% is only 14%-15% of that by evaporation.

Because of the effective separation of magnesium sulfate magnesium nitrate by alcohol crystallization, a nitrate pro-

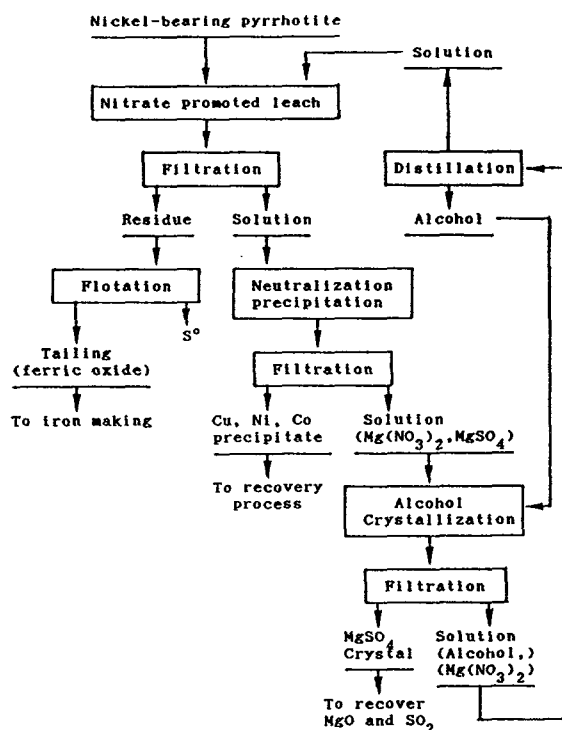


Fig. 1 Principal flowsheet of treatment of nickel-bearing pyrrhotite by nitrate promoted leach.

moted leach process was studied (Fig. 1). Pyrrhotite is leached by nitrate promoted leach. After separating Ni, Cu and Co, the solution, which contains magnesium sulfate and magnesium nitrate, is treated by alcohol crystallization method.  $MgSO_4$  crystallizes out, the spent liquor is sent to distillation to recover alcohol. The solution, which contains magnesium nitrate, is recycled to leaching process. This method has the advantages of nitric acid leach, but no nitric acid consumption.

## 2. PHASE EQUILIBRIA OF THE WATER-COPPER SULFATE- 2-BUTOXYETHANOL SYSTEM WITH SPECIAL INTEREST IN PHASE SEPARATION

There are many binary systems have lower critical solution temperature. Based on this extremely temperature-sensitive character, a salt separation method was proposed.

As shown in Fig. 2, A suitable organic solvent is added to a salt aqueous solution. The system is then cooled down to or below the lower critical solution temperature. In such a case, the organic solvent will fully dissolve into aqueous solution, therefore, the solubility of inorganic salt in the solution will decrease suddenly and most of the salt will crystallize out. After the crystals are separated, the spent liquor is heated to an appropriate temperature above the lower critical solution temperature. Then the solution will divided into two liquid phases again. Thus most of the water and organic solvent are separated from each other and the organic solvent can be reused.

In this research, 2-butoxyethanol was

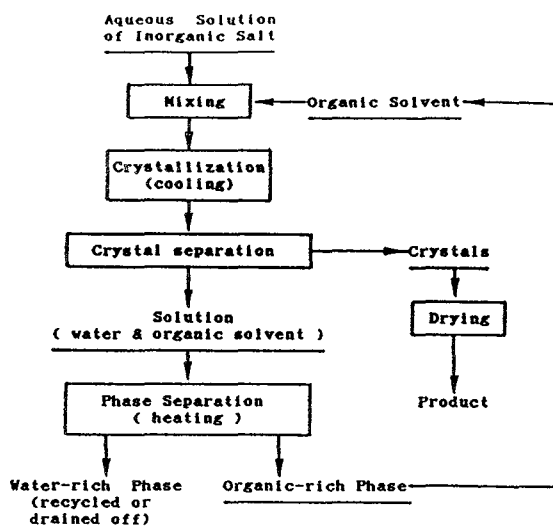


Fig. 2 The proposed flowsheet of new crystallization process.

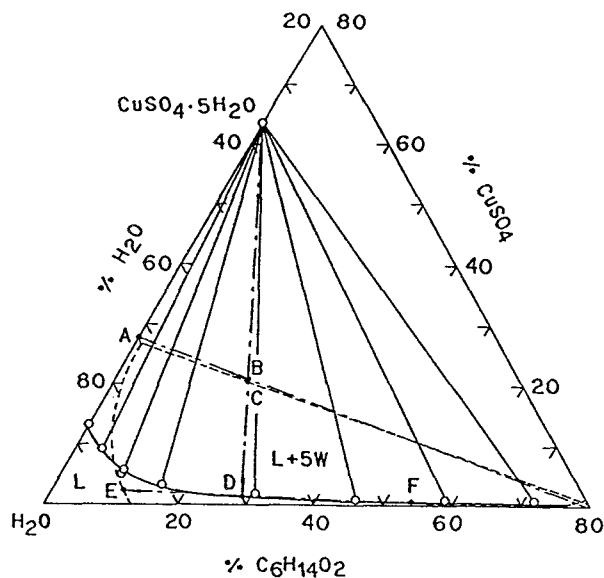


Fig. 3 Isothermal section of the water-2-butoxyethanol-copper sulphate system at 57°C (dotted lines) and at 1°C (solid lines).

selected as organic solvent and copper sulfate as the inorganic salt to be separated. The phase diagram of the water-2-butoxyethanol-copper sulfate system at 57°C (dotted line) and 1°C (solid line) was shown in Fig. 3.

If 80% 2-butoxyethanol is added into a saturated copper sulfate solution A at 57°C until the content of 2-butoxyethanol in the ternary system reaches 20%, the composition of the solution will move to B. In this case, a little copper sulfate will crystallize out and the composition of the solution will change to C, and the solution will divide into two liquid phases. When the system is cooled to 1°C most of the copper sulfate will crystallize out, the composition of the solution shifts to D where the content of copper sulfate in the solution is very low (1.5%).

After crystals of copper sulfate are filtered out from the solution, the temperature of the solution is elevated to 57°C or higher, the solution will separate into a water-rich phase E and an organic solvent-rich phase F. In the water-rich phase, 2-butoxyethanol is less than 8% and copper sulfate is less than 2.5%, while in the organic solvent-rich phase, 2-butoxyethanol is more than 50% and copper sulfate, only trace. Thus, the three components are separated from each other only by varying the temperature within 60 degrees. The energy consumption by this way is about 20% of that by evaporative-crystallization method.

### 3. THE ALCOHOL SEPARATION OF KCl AND NaCl FROM MAGNESIUM CHLORIDE MIXTURES IN MAGNESIUM PRODUCTION

Carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$  or  $NaCl \cdot MgCl_2 \cdot 6H_2O$ ) is an important raw material for magnesium production. Because the presence of alkali metal chlorides in the lattice of hydrous magnesium chloride weakens the bond energy between  $MgCl_2$  and  $H_2O$ , the dehydration of hydrous carnallite is much easier than that of pure hydrous magnesium chloride. After dehydration, anhydrous carnallite can be directly sent to electrolysis cell to produce magnesium. However, a lot of potassium chloride and sodium chloride

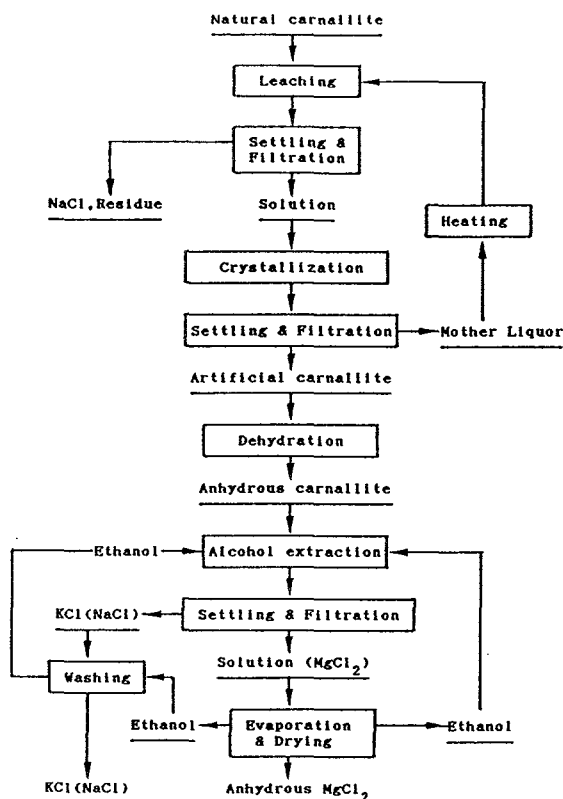


Fig. 4 Flow-sheet for preparing anhydrous  $MgCl_2$  from natural carnallite by Alcohol separation.

will remain in the bath, requiring constantly bleeding off a large amount of electrolyte. Therefore to find a method of separating potassium chloride and sodium chloride from anhydrous carnallite before electrolysis becomes an interesting subject.

Alcohols are important industrial solvents. The solubilities of  $MgCl_2$  in some lower alcohols are rather good. Contrary, the solubilities of  $KCl$  and  $NaCl$  in alcohols are very low and  $KCl$  or  $NaCl$  do not react with alcohol. So alcohols are the most attractive organic solvents. Among them, ethanol is the preferred one for preparing cell feed.

The equilibrium data of the  $MgCl_2$ - $KCl$ - $EtOH$  and  $MgCl_2$ - $NaCl$ - $EtOH$  systems were determined. The ratios of  $MgCl_2/KCl$  and  $MgCl_2/NaCl$  in the solutions increase rapidly with the increase of  $MgCl_2$  content. At co-crystallization points, the ratios of  $MgCl_2/KCl$  reach 5070 at  $70^\circ C$  and 5765 at  $50^\circ C$ ; The ratios of  $MgCl_2/NaCl$  reach 4150 at  $70^\circ C$  and 4300 at  $50^\circ C$ . In other words, the  $KCl$  content in anhydrous  $MgCl_2$  can be theoretically reduced to 0.02-0.018%, the  $NaCl$  content in anhydrous  $MgCl_2$  can be reduced to 0.024-0.023%.

The flow-sheet for preparing anhydrous  $MgCl_2$  from carnallite by alcohol extraction was shown in Fig. 4. After leach and dehydration, anhydrous carnallite was ground and leached with anhydrous ethanol at boiling temperature for 1 hr. After settling and filtration, the residue ( $KCl$ ,  $NaCl$  and  $MgO$ ) was washed with ethanol at room temperature, then washing liquor was recycled to alcohol leaching process. After evaporating ethanol, a white magnesium chloride was obtained, which contained  $MgCl_2$  99.62%,  $MgO$  0.18%,  $KCl$  0.03%  $NaCl$  0.03%, others 0.14%.

#### 4. DEHUMIDIFICATION OF THE $MgCl_2$ - $C_3H_8O_3$ - $H_2O$ AND $LiCl$ - $C_3H_8O_3$ - $H_2O$ SYSTEMS

Humidity of air is an important environment factor in close relationship with human living and industrial production. Dehumidification by hygroscopic liquids is very effective and suitable to treat air on large scale. For air dehumidification, triethylene glycol and lithium chloride solution are in common use.

To improve the dehumidification efficiency of glycerol and triethylene glycol, a method by adding magnesium chloride into glycerol-water system and adding lithium chloride into triethylene glycol-water system to coordinate water has been studied.

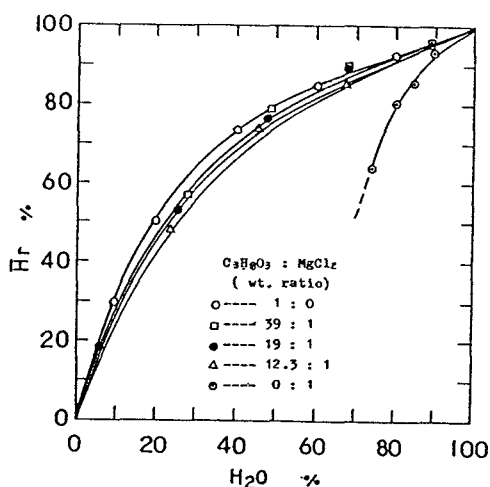


Fig. 5 Relative humidities of the gas in contact with the  $MgCl_2$ - $C_3H_8O_3$ - $H_2O$  system.

The phase diagrams of the  $\text{MgCl}_2\text{-C}_3\text{H}_8\text{O}_3\text{-H}_2\text{O}$  system at  $20^\circ\text{C}$  and  $70^\circ\text{C}$  and the  $\text{LiCl-C}_6\text{H}_{14}\text{O}_4\text{-H}_2\text{O}$  system at  $25^\circ\text{C}$  were determined. Because there are large liquid areas in the ternary system, the suitable operation compositions can be selected in a wide range.

The vapor pressures of the  $\text{MgCl}_2\text{-C}_3\text{H}_8\text{O}_3\text{-H}_2\text{O}$  system at different temperatures were summarized in Fig. 5. When water content is constant, the humidity decreases with the increase of the content of magnesium chloride. For example, the humidity of the gas in contact with a glycerol solution (20%  $\text{H}_2\text{O}$ ) is about 50%, while the humidity of the gas in contact with a solution (20%  $\text{H}_2\text{O}$  and 6%  $\text{MgCl}_2$ ), is only 40%.

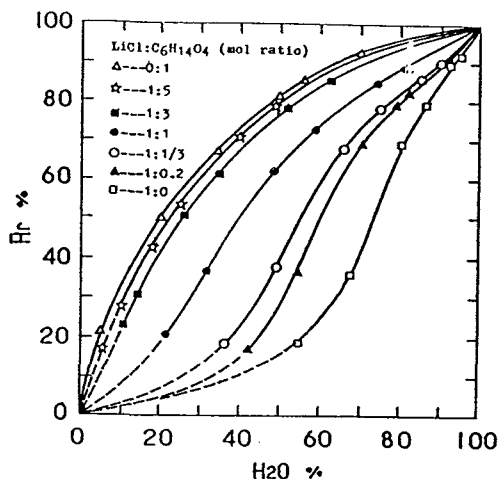


Fig. 6 The average relative humidities of gases in contact with the  $\text{LiCl-C}_6\text{H}_{14}\text{O}_4\text{-H}_2\text{O}$  system.

The average relative humidities of the  $\text{LiCl-C}_6\text{H}_{14}\text{O}_4\text{-H}_2\text{O}$  system were summarized in Fig. 6. Because the mol ratio  $\text{LiCl}/\text{C}_6\text{H}_{14}\text{O}_4$  does not change during dehumidification, the humidities of gases in equilibrium with the solutions will change upward along these lines with the increase of the water contents in the solutions. When water contents are the same, the average relative humidities ( $\overline{Hr}$ ) decrease with the increase of  $\text{LiCl}$  content. For example, the average humidity of the gas in contact with a triethylene glycol solution (20%  $\text{H}_2\text{O}$ ) is 50%, while the average humidity of the gas in contact with a ternary triethylene glycol solution (20%  $\text{H}_2\text{O}$  and 17.6%  $\text{LiCl}$ ) is only 19%.

## 5. DEHYDRATION OF MAGNESIUM CHLORIDE BY BUTANOL DISTILLATION

In magnesium production, hydrate water of magnesium chloride always causes corrosion problem during electrolysis, resulting in high maintenance cost, sludge formation, anode consumption and low current efficiency, therefore, hexahydrate of magnesium chloride must be dehydrated before electrolysis. But hydrous magnesium chloride can not be directly dehydrated by drying or calcining without the formation of magnesium oxide, practically about 50% of the magnesium production cost is charged to the preparation of cell feed, this is primarily due to the high energy consumption in the dehydration of magnesium chloride.

Alcohols are typical polar organic compounds. Some of them can replace water to form coordinates with magnesium chloride, which weakens the binding force between water and magnesium chloride, thus, makes the dehydration of magnesium chloride much easier.

In this research, methanol, ethanol, n-propanol, n-butanol, amyl alcohol and ethylene glycol have been used as organic solvents for the dehydration of hydrous magnesium chloride. The results show that with the increasing of the number of carbon atoms in the molecule of alcohol, the dehydration ability increases. But when higher carbon alcohol is used for dehydration, the distillation has to be carried out at higher temperature. In this case, the reaction between salt and alcohol will occur. Therefore n-butanol was selected.

The boiling points and the compositions of equilibrium gas phase of the  $\text{MgCl}_2\text{-C}_4\text{H}_9\text{OH-H}_2\text{O}$  systems with different concentrations of magnesium chloride and water were determined.

The results are shown in Fig. 7. the solid lines are the boiling points lines. In distillation, if keep the ratios of  $\text{MgCl}_2/\text{BuOH}$  unchanged, the boiling points of the solution will change along these lines when the compositions of the solutions change.

The dotted lines are equilibrium gas phase lines. With the increasing of  $\text{MgCl}_2$  concentration, magnesium chloride fixes more water and therefore the fraction of water in gas phase is less than that in liquid phase. Contrary, when the concentration of  $\text{MgCl}_2$  is lower, the water fraction in gas phase is larger than that in liquid phase. This means that low concentration of magnesium chloride is favorable for the removal of water. Therefore, "distillation" has to be used, and before evaporating the final butanol, water must be reduced to a desirable level, the concentration of magnesium chloride in distilled solution should be kept at some lower level.

A single stage distillation experiment indicated that after 13 times butanol was added, stop adding butanol. With the evaporation of butanol, the temperature was finally increased to  $400^\circ\text{C}$ . The total dewatering reached 97.3%. A white anhydrous magnesium chloride was obtained, in which the content of magnesium oxide was less than 1.5%.

## 6. CONCLUSIONS

Metallurgical industry is one of the largest energy consumers, energy conservation is a hard task for metallurgists. The application of water-soluble solvents to hydrometallurgy is a new metallurgy area. The special characteristics of alcohols offer great opportunity for developing

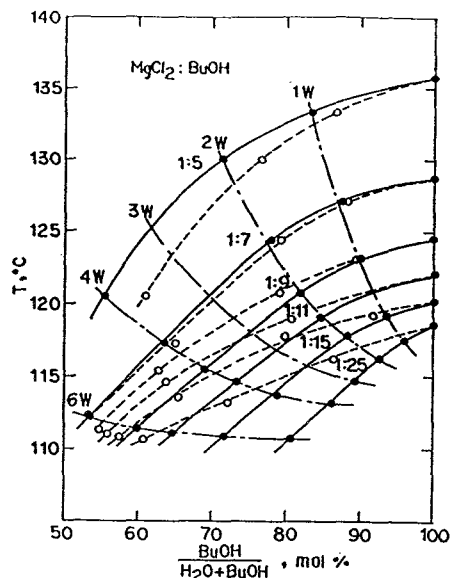


Fig. 7 The gas-liquid equilibria of the  $\text{MgCl}_2\text{-H}_2\text{O-BuOH}$  system with various ratios of  $\text{MgCl}_2:\text{BuOH}$ .

untraditional metallurgical processes. The present studies are from 5 angles to treat the relationships among salts, water and alcohols. From the results, five kind processes were developed.

1) Alcohol crystallization is an effective method for the separation of magnesium nitrate and magnesium sulfate with less energy consumption. From which a nitrate promoted leach process was proposed. It has the advantages of nitric acid leach, but no nitric acid consumption.

2) Based on the phenomena of lower critical solution temperature, a DTE PROCESS (differential temperature extraction) was proposed. The separation of organic solvent, salt and water can be carried out by slight variation of temperature. For tested system, the energy consumption by this way is only about 20% of that by evaporation.

3) Organic solvent purification is an effective method, especially for those process which must be kept away from water. By this method, a pure anhydrous magnesium chloride can be prepared from anhydrous carnallite. The composition of magnesium chloride obtained is  $\text{MgCl}_2$  99.62%,  $\text{MgO}$  0.18%,  $\text{KCl}$  0.03%,  $\text{NaCl}$  0.03% and others 0.14%.

4) In ternary salt-organic solvent-water systems, the strong complex ability of  $\text{MgCl}_2$  and  $\text{LiCl}$  with water can obviously improve the dehumidification of glycerol and triethylene glycol. The relative humidity of the gas in contact with the triethylene glycol solution (20%  $\text{H}_2\text{O}$ ) was 50%, while the average humidity of the gas in contact with the ternary solution (20%  $\text{H}_2\text{O}$ , 17.6%  $\text{LiCl}$  and 62.4%  $\text{C}_6\text{H}_{14}\text{O}_4$ ) decreased to 19%.

5) Some alcohols can form coordinates with magnesium chloride, which weakens the binding force between water and magnesium chloride, and then, makes the dehydration of magnesium chloride easier. By n-butanol distillation method, the overall dewatering reached 97.3%. The white anhydrous magnesium chloride obtained, in which magnesium oxide content was less than 1.5%, is suitable for electrolysis in magnesium production.

The immense varieties of non-aqueous solutions gives us a great opportunity to develop unusual processes for special uses. There are many subjects to be done both in extend research of present works and new process development. NON-AQUEOUS SOLUTION METALLURGY will go through its infancy and possess its reasonable position in extractive metallurgy.



## 審 査 結 果 の 要 旨

金属製錬において目的金属とそれ以外の成分とを分離するための方法の一つとして水溶性に富む溶媒であるアルコール類の利用が考えられるが、その基礎となる金属塩-水-アルコール系に関する従来の研究は不十分で、直ちにアルコール類を利用するには不明確な点が多い。本論文は、濕式製錬における各種の分離操作および塩、空気等の脱水過程にアルコール類を利用する具体的方法について基礎研究を行った結果をまとめたもので、全編7章よりなる。

第1章は緒論であり、本研究の背景と目的について述べている。

第2章ではマグネシアを含むニッケル硫化鉄鉱の硝酸浸出に引続いてアルコール晶析法を適用することを提案し、相平衡測定の結果からエタノールを用いて $\text{MgSO}_4$ を系外に晶析分離すると同時に硝酸を $\text{Mg}(\text{NO}_3)_2$ として回収できることを見出している。これはこの種の難処理鉱石の利用に道を拓く有用な知見である。

第3章は硫酸銅の晶析にアルコールを用いる方法について検討した結果を述べている。各種のアルコールと硫酸銅、水との3元系について相平衡の温度依存性を調べ、硫酸銅飽和温溶液にジブトキシエタノールを加えて冷却することにより、大部分の硫酸銅を晶析できることを明らかにしている。

第4章ではマグネシウム溶融塩電解原料として重要な無水 $\text{MgCl}_2$ 製造にアルコールを利用する方法についての研究結果を述べている。まず、 $\text{MgCl}_2$ に $\text{KCl}$ 、 $\text{NaCl}$ を加えて脱水性のよい無水人工カーナライトを作り、次にアルコールを用いて $\text{KCl}$ 、 $\text{NaCl}$ を晶析分離する方法を考案し、溶解度測定の結果からエタノールを選び、 $\text{KCl}$ 、 $\text{NaCl}$ を効率よく分離し、マグネシウムは無水 $\text{MgCl}_2$ として回収できることを見出している。これは多様な応用が考えられる新しい提案である。

第5章は溶錬用空気の脱湿にアルコールを利用する方法について述べている。その基礎として、グリセロール- $\text{MgCl}_2$ -水系、トリエチレングリコール- $\text{LiCl}$ -水系について平衡水蒸気圧を測定し、これらの3元系を脱湿剤として使用することにより、溶液状態を保ちつつ脱湿効果を向上させ得ることを示している。

第6章は第4章で述べた無水 $\text{MgCl}_2$ の製造方法の別法として、 $\text{MgCl}_2$ そのものの脱水をアルコール添加蒸留によって行う方法について述べている。種々のアルコールについて特性を調べた結果、ブタノールを選び、 $\text{MgCl}_2$ -ブタノール-水系について平衡関係の測定を行った後、繰返し蒸留により無水 $\text{MgCl}_2$ を得ることに成功している。

第7章は結論である。

以上要するに本論文は、金属製錬における種々の分離操作、とくに水溶液を介して塩を晶析分離する操作ならびに脱水過程にアルコール類を利用する新しい方法を提案し、これについて理論的、実験的に検討して実用への基礎を与えたもので、金属工学の発展に寄与するところが少なくない。

よって、本論文は工学博士の学位論文として合格と認める。