

Composite copper powder from Kelex 100

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Kelex100로부터 구리입자 분말 합성

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Abstract A composite copper coated powder was generated by pressure hydrogen stripping copper from Kelex 100 solvent extractant in the presence of silica powder. Within the limitation of solvent extraction under constant conditions, both loading level and stripping rate were reproducible. The stripping copper kinetics are reduced from a divalent state to a metallic state and then deposited on the surface of the silica powder. Copper nucleates heterogeneously on the seed particles. They are giving an agglomerated and non-uniform powder.

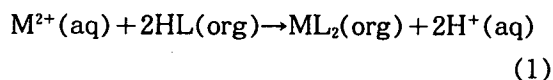
요 약 구리입자를 코팅한 분말 합성은 Kelex 100 solvent extraction으로부터 silica powder에 수소압력 stripping copper에 의하여 생성하였다. Solvent extraction의 범위내인 일정한 조건에서 loading level 과 stripping rate등을 재생하였으며 stripping copper kinetics는 divalent 상태에서 metallic 상태로 감소하면서 silica 입자에 침적하였다. Copper들은 seed 입자에 heterogeneous 핵을 형성하면서 이들은 agglomeration상태로 생성되었고 불균일한 분말로 형성하였다.

1. Introduction

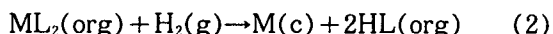
Pressure hydrogen stripping of solvent extractions is an alternative to conventional aqueous-based stripping, allowing direct metal coated powder production from the organic phase. The applicability of hydrogen stripping is restricted to systems in which the organic structure is stable under the necessary for metal precipitation, and to metals amenable to hydrogen reduction in aqueous media. Pressure hydrogen stripping of copper, nickel, and cobalt from versatic 911 and Diethylhexylphosphoric acid was examined by Burkin and Burgess [1]. Van der zeeuw and Gandon studied the reduction of copper and nickel in versatic acids at atmospheric hydrogen pressure [2]. In addition, the technique has been successfully tested for copper, nickel, and cobalt from chelating extractions (Kelex 100 and LIX 65N) [3-10].

Although pressure hydrogen stripping may require higher temperatures than comparable aqueous systems, the specific heat of the organic system is approximately half of that of aqueous systems [3]. Sherrit-Gordon uses hydrogen reduction from aqueous ammoniac solutions for the recovery of nickel. This system operates an autoclave between 170°C and 205°C with a total system pressure of 450 psig [11,12]. The ability to strip nickel from kelex 100 at 250°C with a hydrogen pressure of 200 psig was demonstrated by Destin [4,11,12].

The study of pressure hydrogen stripping of a particular organic/metal system involves the stability of the organic extraction, the homogeneous or heterogeneous reaction kinetics of the metal reduction, and the properties of the powder produced [4,5,13]. The main reaction of a divalent metal loading can be written by;



Reduction of the metal can be represented by;



Based on the experimental observations, a reaction mechanism is proposed in an effort to describe each of the observed effects and gain a better understanding of the parameters involved.

2. Experimental Procedures

Stripping experiment was carried out using 0.4 M Kelex 100 (15 vol. %), 10 % Decyl Alcohol (99 % pure), and 75 % deodorized Kerosene. The cupric solution was prepared using reagent grade copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 58.94 g/l) to make a solution of 15 g/l copper. Standard laboratory grade hydrogen and argon gases were used for washing equipment, and reagent grade acetone was used for washing the powder.

Hydrogen stripping was carried out using 500 ml stainless steel, and low-pressure autoclave. The system pressure was monitored using an Omega PX 102 pressure transducer with a range from 0 to 1000 psig. The temperature was monitored using type K thermocouples with digital display (see Fig. 1). Kelex 100 was loaded with copper by combining equal amounts (200 ml each) of stock extraction and cupric solutions. The extraction conditions were standardized to sixty minutes with an agitation rate of approximately two hundred cycles per minute, and carried out at room temperature without pH control. To minimize the amount of aqueous phase entering the autoclave, aqueous was drawn off at three time intervals (15, 10, and 5 minutes). After phase separation the loaded kelex 100 was changed directly into the autoclave, followed by seed addition, and insertion of the baffle bar. The autoclave was then sealed, the agitator set at 600 rpm, and the autoclave purged ten times with standard lab-

oratory grade argon (20 psig). The agitator speed was increased to 1000 rpm and the autoclave brought to the desired temperature (maintained $\pm 1^\circ\text{C}$). The contents were heated to the desired reaction temperatures. At the end of a test, the system was cooled under hydrogen to room temperature. The product was filtered and washed in acetone. Studies of the copper coated powder comprised physical and chemical examination by conventional instrumental methods.

3. Results and Discussion

Experiments investigated the behavior of hydrogen stripping system; seed material type, seed quantity, temperature, hydrogen pressure, initial copper concentration, and initial free kelex 100 concentration. In addition to investigating the hydrogen stripping kinetics, the powder size and morphology were characterized in an attempt to determine the usefulness of the product. The pressure change was assumed to follow the ideal gas law. The pressure change was directly proportional to the molar change. The pressure drop over time was thus used to calculate the amount of copper stripped over time. This relationship was used to present the kinetic data in Figs. The pressure/mole relationship should be approximated by the ideal gas law over the relatively small pressure drops observed; a typical pressure drop was 40 psig H_2 out of 600 psig

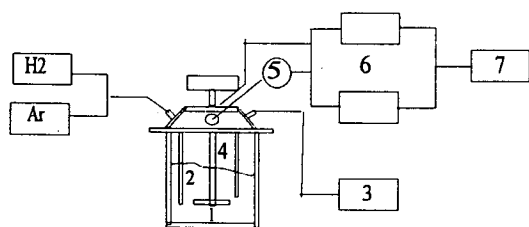


Fig. 1. Schematic of the experiment system. 1) agitator, 2) gas inlet, 3) gas outlet, 4) thermocouple, 5) pressure transducer, 6) digital display in temperature and pressure, 7) recoding system.

total system pressure, less than a seven percent charge.

3.1. Seed material and amount effect

The effect of different seed materials, compared to no seed, is shown in Fig. 2. The addition of seed material enhances the kinetics over that of no seed addition. Considerable interest has been shown in composite powders such as copper coated tungsten carbide (electrical contacts) and copper coated tungsten (electronic packing). In order to coat a powdered substrate in solution, the powder must be well suspended to provide deposition sites. Silica was selected as the standard seed material because it has a low density (easy to suspend).

The rate of hydrogen stripping with increasing amount of seed presents in Fig. 3. By adding increasing amounts of silica up to one gram, the rate of the reaction increases. Since an increase in stripping rate between one and two grams silica is not much different, this suggests a change in controlling mechanism. The rate of copper deposition depends on the rate of

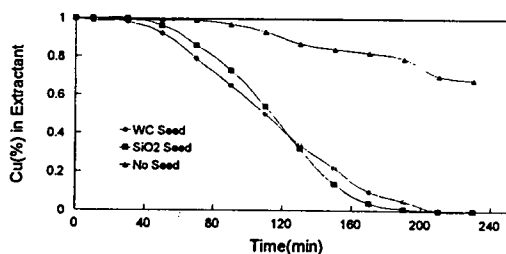


Fig. 2. The effect of seed(2 g)(200C, 384 psig H₂).

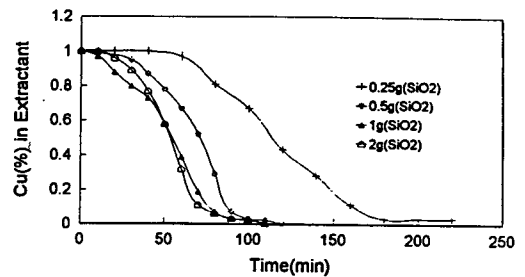


Fig. 3. Increasing amount of seed(200C, 585 psig H₂).

mass transfer to the particle, which depends on the surface area available and the concentration of molecular copper present. The mass transfer of a particle may be represented by

$$\{n_{Cu}\}/\{A*t\} = h_m[Cu](mol) \quad (3)$$

where h_m is the mass transfer coefficient for copper, n_{Cu} is the moles copper transferred, A is the surface, and t is the time. Thus, the growth of the particle may be represented by

$$\{-d((4/3)D(r_i)^3P_{Cu})\}/dt = 4D(r_i)^2h_m[Cu] \quad (mol) \quad (4)$$

where r_i is the instantaneous radius, r_0 is the initial radius ($r_i = r_0$ ($t = 0$)), and P_{Cu} is the copper density.

This effect was observed in Fig. 3. The rate of growth is also dependent on the concentration of molecular copper available for deposition. Since the concentration of copper is dependent on the reaction, it is dependent on temperature and concentration of the reactants and prod-