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Recovering of Copper from Synthetic Solution in 3PE Reactor

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ABSTRACT Recovery of copper from a synthetic solution with an initial copper concentration 1 g/l, pH 1 was investigated in a Pulsed Porous Percolated Electrode reactor (3PE). This reactor was constructed in the axial field configuration with 0.2 m diameter and 0.35 m height. Graphite particles were used as a voluminal cathode and a counter electrode made of titanium coated with ruthenium oxide was placed 0.04 - 0.05 m above the upper level of carbon particles. The optimum current intensity was obtained at 9 A at which more than 90 % of copper was recovered in 4 hours. Due to a current intensity drop during the destabilization of the granular bed, the recovery rate of copper decreased when the pulse frequency increased. In addition, a reasonable operating cost was obtained at about 14.87 FF/m^3 (1.97 US\$/m^3) at optimum current. A dimensionless number, which shows the relationship between the mass transfer coefficient and flow rate of the electrolyte, was defined.

KEYWORDS: Copper, Recovery, 3PE reactor, Electrodeposition technique.

INTRODUCTION

Metals contamination in processed water is a serious problem for several industrial sectors such as surface treatment, electroplating and the electronics industry. The outlet wastewater from these industrial processes normally contains a metal concentration higher than the acceptable limit set by law. Therefore, the treatment of contaminated water before it is directly discharged is required in order to reduce the amount of metal to an acceptable level.

The prospect of recovery has attracted interest among industries for environmental and economic reasons. For example, valuable heavy metals are recycled and reused while the outlet water is permitted to discharge to the environment. Many previous studies have attempted to find reasonable ways to recover heavy metals. Electrochemical process has low sludge production, low start-up and operating cost, no chemical contamination in the treated water, and high recovery of separated metals and processing materials.

A multi-stage process has been investigated to recover heavy metals of Cu, Ni and Cr.[1-2] Metal contaminated wastewater was first treated biologically, then by an acid leaching treatment and finally by an electrochemical treatment. Armstrong[3] reported the feasibility of selective electrodeposition of cadmium, cobalt, and nickel from a binary mixture as ~99 % pure metals. They pointed out that Cd(II) could be electrodeposited from a solution containing Cd(II) and Co(II) or Ni(II) without codeposition of Co and Ni.

The electrodeposition process is carried out utilizing a three-dimensional electrode for its high active surface area per unit volume and high efficiency in mass transfer. Panizza[4] used a copper foam electrode to remove copper from industrial effluent in an undivided mono-polar cell. The percent removed was greater than 98 % with a flow rate 1000 l/h at current intensity of 750 A. In other work by Polcara[5], a recirculating batch reactor consisting of carbon felt electrodes held on an anionic exchange membrane was used to remove and recover heavy metal pollutants. About 90 % of the mercury was deposited on the electrode surface. Concentrations of copper and lead were reduced from 50 ppm to 0.05 ppm with 42 % current efficiency at -300 mV/SCE (Saturated Calomel Electrode) for copper and from 100 ppm to 1 ppm with 25 % current efficiency at -600 mV/SCE for lead.

A new type of electrochemical reactor named 3PE reactor (Pulsed Porous Percolated Electrode) was patented and constructed on an industrial scale.[6-7] Fenouillet et al[8] used this reactor in the axial field configuration to recover copper. Copper had been recovered until its final concentration was lower than 2 ppm. Reussard et al[9] demonstrated the removal of chromium in 3PE reactor with a radial field configuration. They pointed out that the pH changed versus time during electrolysis and 100 % conversion was reached with controled pH. Aguirre et al[10] described results of metal recovery from electroplating effluent in 3PE reactor. They found that the percentage of recovered copper, zinc and nickel was about 99, 93 and 80 % in 9, 13 and 16 hr, respectively.

This paper describes the effect of parameters (current intensity, pulse frequency, cathode type and flow rate of solution) on copper recovery in 3PE reactor. A synthetic solution was used to eliminate other parameters. The effect of potential between working and reference electrodes was not studied because in industry the operating control is more difficult. A dimensionless number for this system was developed to describe the functioning of the reactor.

MATERIALS AND METHODS

The 3PE reactor can be considered as a compromise between fixed and fluidized bed reactors. It is composed of four components[10]:

A. *A solid matrix*, composed of particles that act as voluminal cathode in contact with the current feeder.

B. *A counter electrode* or anode having a small geometrical surface area. The material used must be resistant to oxidizing conditions. Platinum or titanium coated with ruthenium oxide are good choices.

C. *A circulation pump* is used to circulate the electrolyte in the system through the granular bed. Two advantages of this are the renewal of the solution around the particles and structural improvement of the metal layer deposited.

D. *A pulsating system* creates movement of the granular bed in the reactor forcing the movement of metal-coated particles to the bottom of the bed and avoiding the problem of clogging.

During the operation, when the current is applied through the solution, the potential gradient is created at the terminals of the electrode. The metal ions in solution are reduced to the metallic state and deposited onto the surface of the particles which face the anode (during (1-ξ)τ period) as shown in figure 1. The behavior of particles at this moment is similar to a fixed bed.

When the air pulsation is applied, good contact between fluid and particles is obtained. The metal-coated particles, which have high density and weight, fall to the bottom of the reactor by force of gravity and are replaced by new particles during the destabilization period, ξτ. The behavior of these particles during this time period resembles a fluidized bed.

Mass transfer in 3PE reactor

The assumption of material balance is that a well-mixed condition is obtained in the batch reactor, see Figure 2. Material balance of component i in the reactor is expressed by.[11]

$$QC_{iE} = QC_{iS} + \gamma A \qquad (1)$$

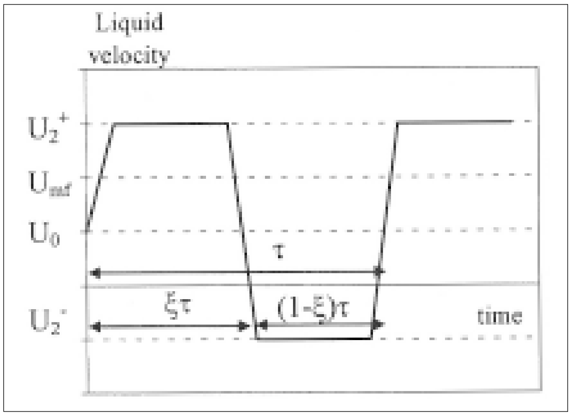

Fig 1. The periodic destabilization of the graphite particles.

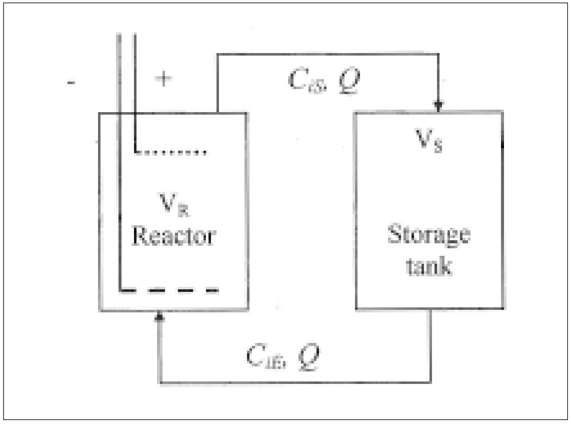

Fig 2. Diagram of apparatus.

$$Q(C_{iE} - C_{iS}) = \gamma A = \frac{j}{nF}\eta A \qquad (2)$$

Given $n = 1$ and $j = nFk_LC_{iS}$, then,

$$\begin{aligned} Q(C_{iE} - C_{iS}) &= \frac{j}{nF} A \\ &= k_L A_e V_e C_{iS} \qquad (3) \end{aligned}$$

If the storage tank is considered as a continuous stirrer tank reactor, the concentration evolution is a function of operating time. The material balance in the storage tank can be expressed by

$$Q(C_{iS} - C_{iE}) = V_S \frac{dC_{iS}}{dt} \qquad (4)$$

The equation (4) can be written as

$$\begin{aligned} Q(C_{iE} - C_{iS}) &= - V_S \frac{dC_{iS}}{dt} \\ &= k_L A_e V_e C_{iS} \qquad (5) \end{aligned}$$

Rearrangement of equation (5), then gives

$$\frac{dC_{iS}}{C_{iS}} = -\left(\frac{k_L A_e V_e}{V_S}\right) dt \qquad (6)$$

We then integrate (equation (7)) to obtain equation (8).

$$\int_{C_0}^{C_t} \frac{\mathrm{dC_{iS}}}{\mathrm{C_{iS}}} = -\left(\frac{\mathrm{k_L A_e V_e}}{\mathrm{V_S}}\right) \int_0^t \mathrm{dt} \qquad (7)$$

$$\ln \frac{C_{it}}{C_{i0}} = -\left(\frac{k_L A_e V_e}{V_S}\right) t \qquad (8)$$

From equation (8), the value of mass transfer coefficient (k_L) can be calculated from the slope of the plot between $\ln(C_{it}/C_{i0})$ and time.

Dimensionless number in 3PE reactor

A dimensionless number which shows the relation between flow rate of electrolyte, mass transfer coefficient, and fluid properties, is expressed in terms of Reynolds numbers of the particular bed, Re_p, Sherwood number, *Sh*, and Schmidt number, *Sc*.

$$\text{Reynolds number } \mathrm{Re}_p = \frac{\rho d_p v}{\mu} \qquad (9)$$

$$\text{Sherwood number } Sh = \frac{k_L d_p}{D} \qquad (10)$$

$$\text{Schmidt number } Sc = \frac{\mu}{\rho D} \qquad (11)$$

The relationship between these three dimensionless numbers can be expressed by the following equation

$$Sh = a \, \mathrm{Re}_p^{\ b} \, Sc^c \qquad (12)$$

where a, b and c are constant. Generally, the value of c is assumed at about 0.25 in the volumetric electrode process.

EXPERIMENTAL

Experiments were performed at laboratory scale and 25 °C with a synthetic solution of copper. The synthetic copper solution, with total volume of 15 litres, was prepared with $CuSO_4{\cdot}5H_2O$ (98 % purity, Fluka Chemica) and adjusted pH by conc.H_2SO_4 (BDH Laboratory Supplies) to pH = 1 for each experiment. The experimental pH of the solution was set equal to 1 in order to eliminate the effect of high pH at the cathode where the evolution of H_2 takes place. The physical properties of copper solution were obtained from the Handbook of Electrolyte solution Part A.[12] The diffusion coefficient was 5.89×10^{-10} m^2/s and the value of density and dynamic viscosity were 1005.6 kg/m^3 and 9.29×10^{-4} kg/m-s; hence, the Schmidt number was about 1568.

The experimental set-up is shown in Figure 3. The 3PE reactor was constructed in the axial field configuration about 0.2 m in diameter and 0.35 m in height. 0.5 kg of graphite particles, 0.0035 m

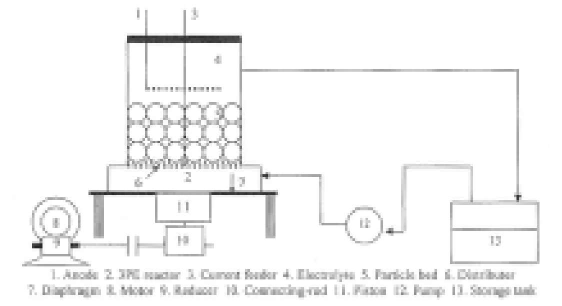

Fig 3. Experimental set up of 3PE reactor with axial field configuration.

diameter, 1690 kg/m^3 density, and 1,000 m^2/m^3 total surface area per unit volume were used as the cathode because Aguirre[10] has tested and demonstrated that the best support for metal deposition are graphite particles used in energy production. A counter electrode or anode made of titanium and coated with ruthenium oxide was placed above the upper level of particles by about 0.04 – 0.05 m to keep the cell voltage within the range of power supply. Its terminal was connected to a regulated power supply type PNT 32-40 (Heizinger). One magnetic pump type MD-20R (Iwaki) was used to circulate the electrolyte between the storage tank and reactor. The pulsation of the system was conducted by an automatic controller of air (apparatus number 8-11 in figure 3). The operation of this controller was similar to a sinusoidal wave.

The process was operated in galvanostatic mode (constant current). The solution was sampled every 2 hr until more than 99 % of copper was recovered. The concentration of copper in the samples was measured by a type (AA-275 Varian) Atomic Absorption Spectrophotometer .

The parameters studied were current intensity (5 - 11 A), flow rate of electrolyte (3 - 8 l/min), pulse frequency (0.16 - 0.43 Hz), cathode type (graphite and graphite covered by copper). The amplitude of pulse was fixed at 0.025 m in order to investigate the effect of other parameters.

Calculation of some parameters

Percent recovery and current efficiency can be calculated by the following equation.

$$\%\, recovery = \frac{\left(W_i - W_t\right)}{W_i} x100 \qquad (13)$$

$$\%\, current\ efficiency = \frac{nFW_i\,(\%\, recovery)}{MW(it)} \qquad (14)$$

$$Operating\ cost = \frac{itVC_u}{V_T} \qquad (15)$$

RESULTS AND DISCUSSION

Optimum Current Intensity

The current intensity was varied between 5 - 11 A at a constant flow rate of electrolyte (8.4 l/min) of synthetic copper solution with initial concentration of 1 g/l at pH = 1. The effect of current intensity is shown in Figure 4. The electrolysis time decreased when the applied current intensity increased up until 9 A. After that, it had no effect on electrolysis time.

Figure 5 presents the correlation of current efficiency and operating cost as a function of current intensity. The operating cost was calculated by equation (15) after 99 % recovery. The results show that copper is recovered with high efficiency in a 3PE reactor. Copper ions in solution were reduced to the metallic state and deposited on the surface of graphite particles.

The optimum current intensity was obtained at 9 A with more than 90 % recovery in 4 hours and about 35 % of current efficiency. A minimum operating cost of about 14.87 FF/m^3 (1.97 US\$/m^3) was obtained at the optimum current intensity.

Pulse Frequency

The effect of pulse frequency was tested at constant flow rate of electrolytes. Pulse frequencies were varied between 0.16 - 0.43 Hz for copper with

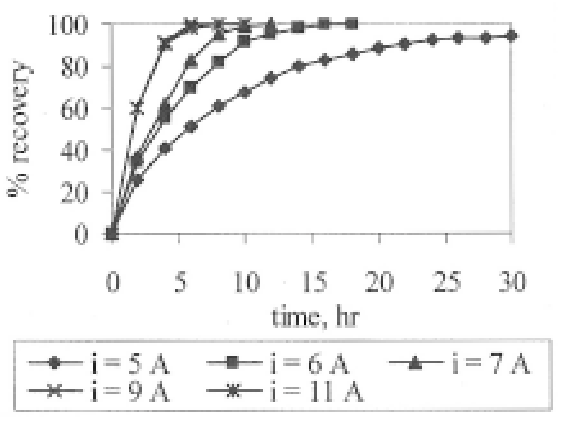

Fig 4. Percent recovery versus time of copper solution 1 g/l, pH = 1.

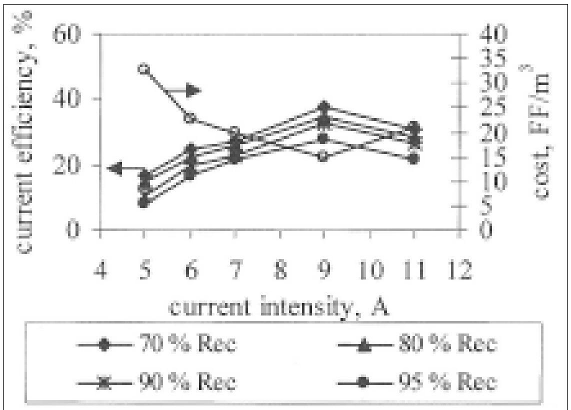

Fig 5. Current efficiency and operating cost versus current intensity of copper solution 1 g/l, pH = 1.

initial concentration 1 g/l, pH = 1, flow rate 8 l/min, and 9 A of current intensity.

The effect of pulse frequency is shown in Figure 6. Results show that when the pulse frequency is increased, the copper recovery rate decreases. This is because destabilization of the bed occurs disrupting the contact between particles and between particles and the current feeder. The current between the anodic and cathodic is hindered causing a drop in current intensity.

Because of the better contact at low pulse frequency, a higher percentage of recovery is obtained. Although a high metal recovery is obtained at a pulse frequency of about 0.16 Hz, a bridge between adjacent particles is observed. If the experiment is performed at pulse frequency lower than 0.16 Hz, there is a problem with clogging. Experiments were not performed at a pulse frequency less than 0.16 Hz.

Influence of Cathode Composition

In previous experiments in which graphite particles were used as a cathode, copper ions reduced to metallic state were initially deposited on the graphite surface of the particles. After this point, the reaction was continuous as the metallic copper deposited on graphite already covered by copper. This is similar to deposition of copper ions on metallic copper. When the experiment was over, the graphite particles were refreshed by a rinse in nitric acid (HNO_3, BDH Laboratory Supplies).

In this case, experiments to determine the effect of cathode composition were conducted by cyclic voltammetry using a Potentiostat/ Galvanostat Apparatus Model 273. Graphite and copper rotating disc electrodes were used as the cathode and platinum was used as the anode. The polarization curve showed that the copper cathode consumed an applied current intensity 3 times higher than the graphite cathode. Therefore, the deposition of copper on a copper surface seemed to be higher than on a graphite surface.

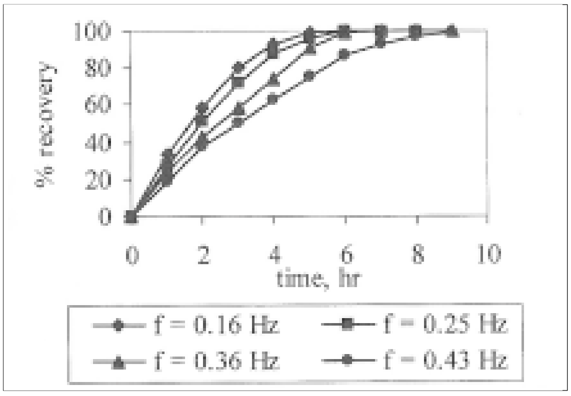

Fig 6. Percent recovery versus time of copper 1 g/l, pH = 1, i = 9 A.

However, in a 3PE reactor, the results of concentration evolution with two types of cathode surface (graphite and graphite covered by metallic copper) indicated that the concentration evolution of copper on the two types of cathode had the same behavior. Copper ions in solution were completely recovered in about 7 hours. It can be concluded that the surface composition had no affect on the copper deposition process. In this study, with the applied current intensity being greater than the limiting current intensity, there was a sufficiency of charge to deposit on both surfaces.

Flow Rate of Solution

The experiments of copper 1 g/l, pH = 1 at optimum current intensity (i = 9 A) were performed at different flow rates (3 - 8 l/min).

Figure 7 shows the results of these experiments. The percent recovery increased with flow rate because the higher the flow rate, the higher the mass transfer of metal species present.

The mass transfer coefficient, k_L, for each flow rate was determined by equation (8). The concentration included in this determination ranged between 50 - 1,000 mg/l because the atomic absorption spectrophotometer gave low precision at very low concentration. The results indicated that when flow rate increased, k_L increased.

Following these results, a dimensionless number that shows the relationship between the mass transfer coefficient, flow rate of electrolyte, and physical properties of solution was developed in terms of the Sherwood number according to equation (12). It can be expressed by the following equation.

$$Sh = 1.20\ \mathrm{Re}_p^{0.411}\ Sc^{0.25}$$

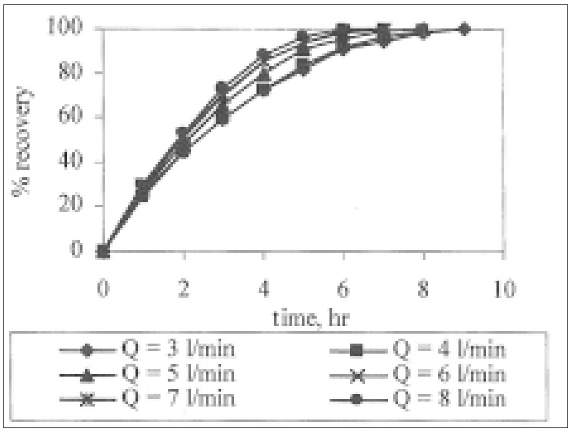

Fig 7. Percent recovery versus time of copper 1 g/l, pH = 1, i = 9 A.

When $6 < Re_p < 16$ and $Sc = 1568$. This dimensionless number is useful for describing the functioning of the reactor and for the scale up of the reactor in further work.

V. Comparison with other works

Figure 8 shows a comparison between our work and the literature.[13-14] Both researchers used an electrochemical technique. The copper recovery system of Olive and Lacost[13] used a flow through porous electrode with spherical particles covered with copper and percolated by a dilute sulfuric acid solution of copper ions. Karabelas[14] used a packed bed reactor to find the mass transfer by using potassium ferrocyanide and potassium ferricyanide.

The results showed that the mass transfer in this work agreed well with these previous studies. The differences may result from the different chemical substances used and the system.

CONCLUSION

From this study, copper ions in synthetic solution were recovered with good efficiency. Optimum current intensity was found at 9 A, at which more than 90 % of copper was recovered in 4 hours. The current efficiency was about 35 % at 90 % recovery. The lowest operating cost was obtained at current intensity of 9 A with about 14.87 FF/m^3 (1.97 US\$/m^3) of treated solution.

Low pulse frequency gave a better percentage of recovery than high pulse frequency due to a current intensity drop during the destabilization of granular particles in the reactor.

Cathode composition, graphite or graphite covered by metallic copper, did not affect the concentration evolution behavior due to the applied current intensity higher than limiting current intensity. In both cases, the complete recovery was achieved in 7 hours.

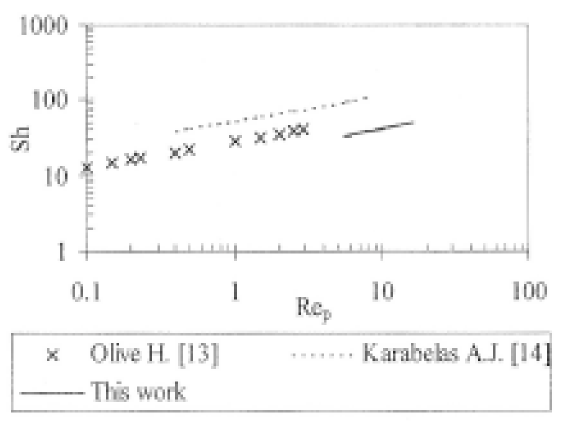

Fig 8. Comparison between our dimensionless number and literature.

Mass transfer coefficients were strongly affected by flow rate of electrolyte. They increased when flow rates increased.

The novelty of this work is the use of an air pulsation system, which prevents clogging by granules and the use of material having high specific surface area as cathode. In addition, a dimensionless number, which shows important relationships regarding reactor functioning was reported. This Reynolds number range is different from the other previous works.

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Nomenclature

A	active area of cathode, m^2 $A = A_e V_e$
A_e	specific surface area per unit volume of cathode, m^{-1}, $A_e = H_p\Omega$
C_{iE}, C_{iS}	inlet and outlet concentration of species i, mol/m^3
C_{it}	concentration of species i at t, mol/m^3
C_{i0}	intial concentration of species i, mol/m^3
C_u	cost of electricity per unit, (= 0.7 FF/kW-hr)
D	diffusion coefficient, m^2/s
d_p	particle diameter, m
f	pulse frequency, Hz
F	Faraday constant, 96500 A-s/equiv
H_p	height of cathode level, m
i	current intensity, A
j	current density, A/m^2
k_L	mass transfer coefficient, m/s
n	number of electron involved in the system
Q	flow rate of solution, m^3/s
t	electrolysis time, s
U_2^+, U_2^-	upward and downward final velocity, m/s
U_{mf}	minimal particle fluidization velocity, m/s
U_0	permanent liquid velocity, m/s
v	velocity of electrolyte, m/s
V	voltage, volt
V_e	total particle volume, m^3
V_R	volume of reactor, m^3
V_S	volume of storage tank, m^3

V_T	volume of solution in reactor and storage tank, m^3, $V_T = V_S + V_R$
W_i	initial weight of metal, g
MW	molecular weight of metal, g
W_t	weight of metal at time t, g

Greek characters

$\xi\tau$	time of destabilized bed, s
$(1-\xi)\tau$	time of fixed bed, s
γ	rate of reaction, mol/s
η	current efficiency
Ω	cross sectional area of reactor, m^2
μ	liquid viscosity, kg/m-s
ρ	liquid density, kg/m^3

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