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Increasing silver leaching rate from leaching-resistant zinc residues by thiourea leaching method with pressurized preoxidation process①

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Abstract: As for the leaching-resistant zinc residues, the silver leaching rate can be over 98% through the process of pressurized preoxidation and thiourea leaching. Compared with the method of extracting the silver directly from the leaching-resistant zinc residues, the silver leaching rate is greatly improved. The optimum preoxidation conditions are: particle size range 40 - 60 μm, oxygen partial pressure 10^6 Pa, temperature 80 - 90 ℃, pH = 1.0, and leaching time 5 h. After pretreatment, the time of thiourea leaching silver is shortened to 1.5 h, and the thiourea consumption is reduced greatly. The oxidation mechanism and the thiourea leaching kinetics were also explored.

Key words: zinc residue; pressurized preoxidation; thiourea leaching; shrinking core model
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1 INTRODUCTION

At present, zinc is produced by the hydrometallurgy-electroanalysis method in most zinc smelting plants. Each year, millions tons of hydrometallurgical zinc residues are discharged from Chinese smelting plants, which are highly acidic and consist of great deal of silver and other valuable metals such as Zn, Pb and Cu. The existing status of the valuable metals are complicated including the nature metal, sulfide, sulphate, halide, oxide, silicate and so on. The silver among the zinc residues mainly exists as the argentic sulfide and the natural form, which will hinder the silver extracting process considerably by using the leaching agents for the reasons of complex physical phases and serious packing effects.

Thiourea, for its well-known capability in leaching noble metals, has become the best substitute for cyanide and is widely used and studied in the extraction of noble metals[1, 2]. Researches were carried out on leaching silver from leaching-resistant zinc residues by the thiourea[3-6]. If leaching the silver directly from the zinc residues by acidic thiourea solution, 86.69% leaching rate could be obtained under pH = 2.0 - 2.5, temperature of 40 - 60 ℃ and leaching time of 2 - 3 h. The argentic sulfide and natural silver in the zinc residues have serious packing effects, which results in a long leaching time and large thiourea waste. In consequence, the economic benefit is affected.

Recovery of silver from the hydrometallurgical zinc residues by acidic thiourea method was studied as well by foreign researchers[7]. In 1980s, a patent of extracting silver from refined zinc residues by acidic thiourea method was issued in Belgium, in which the optimum condition was pH = 2.0, ρ(TU) = 20 g/L, φ(solid) : φ(liquid) = 6 - 7 : 1, temperature 85 ℃, leaching time 3 h, silver leaching rate 85.8%. A patent from Europe reported that a kind of silver recycling process invented by Lucia et al was suitable for most hydrometallurgical zinc smelting plants, and had few influences on original technological process. This silver recycling process can recycle silver from calcine and leached residues. The detailed process was to leach the calcine, intermediate leached residues or low acidic leached residues from the solution of thiourea and sulphate under the ordinary pressure with the leaching conditions at thiourea concentration of 0.1 - 20 g/L, temperature of 30 - 80 ℃, pH 1 - 5, and leaching rate of 85%. Furthermore, many researches are also reported in China and other countries. For examples, Groenewald have studied the mechanism of the silver leaching by thiourea[8]. Pyper and Hendrix have compared the cyaniding method with the thiourea method[9]. In domestic, ZHANG[10] and LI[11] have also developed related studies.

The research works introduced above have the same

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disadvantages as ours, which are of long leaching time, high thiourea consumption and low leaching rate by direct acidic thiourea leaching method. Therefore, leaching the zinc residues directly by thiourea is unsuitable. The zinc residues must be pretreated before it is put into use.

2 EXPERIMENTAL

2.1 Raw materials

In the experiment, the zinc residues will turn into representative samples after the processes of blending and cutting down. Then heat and solve the samples by chloronitric acid and analyze it with spectrophotometer (HITACHI, Z-8000). The chemical analysis result of the sample is listed in Table 1 and the result of physical phases of Ag analyzed by chemical mineralogical analysis method is listed in Table 2. The crystal form and crystal composition of the zinc residues are analyzed by X-ray diffraction instrument (SIEMENS, D5000). The above analysis results show that: 1) the silver content is 488.49 g/t; 2) Approximately 80% silver in the zinc residues exist as Ag_2S or AgCuS, which is thickly packed by ZnS, PbS, CuS, Cu_7S_4, Fe_3O_4 and FeS; 3) Other forms of silver such as natural silver, silver oxide, and arsenical silver etc are packed by those sulfide minerals as well. So, it is a kind of typical leaching-resistant zinc residues in which the sulfides must be oxidized first in order to extract silvers efficiently. The experiment is carried out in two steps: preoxidation process and thiourea leaching process.

Table 1 Analysis result of raw material elements

Element	Ag	Zn	Pb	Cu	Fe	S	SO_2	SiO_2
Content /%	0.049	20.45	4.17	0.486	19.59	8.35	6.08	> 40

Table 2 Physical phase analysis result of raw material

Mineral	Content/(g·t^{-1})	Distribution rate/%
Ag_2SO_4	1.455	0.30
Ag_2O	41	8.45
Ag_2S	386	79.59
Ag	14	2.89
Others	42.545	8.77
Total	485	100

2.2 Instruments and procedures

Firstly, grind up the hydrometallurgical zinc residues with laboratory scale ball mill to meet the leaching requirement of the experiment. Secondly, perform the pressurized preoxidation process to extrude the air or oxygen from a high-pressure bottle with an autoclave, which has heating and stirring instruments (GS-2, produced by the Fourth Instrument and Meter Plant of Dalian, China). In the preoxidation experiment, the effects of particle size, temperature, time and partial oxygen pressure on silver leaching rate were studied.

After the preoxidation experiment, the samples were transferred into a beaker to go on the leaching experiment by thiourea under ordinary pressurizing, heating and stirring conditions. In the experiment, the effects of stirring velocity, solid content, leaching time, temperature, thiourea concentration, pH and Fe^{3+} concentration on the leaching rate of Ag were also investigated. The silver analysis was still carried out by atomic absorption spectrophotometer (HITACHI, Z-8000).

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Preoxidation process

The effects of several parameters, such as particle size, partial oxygen pressure, temperature and time on the preoxidation process were studied in the experiment so as to get the optimum oxidation conditions.

3.1.1 Effect of particle size

As shown in Table 3, the particle size has an explicit influence on the leaching rate of silver and it is less than 50% with particle size larger than 80 μm and more than 98% with the size of 40 - 80 μm. It is conceivable that the larger silver particles have more serious packing effect, which makes the particles harder to be disintegrated and decreases the silver-recycling rate. On the other hand, the particles should not be over ground up because the surface activation energy of the superfine particle will thus be increased to make the process of homogeneous wettability on the liquid phase to be more difficult that will affect the leaching reaction accordingly. Furthermore, too tiny particles are excessively easy to coagulate and flocculate.

Table 3 Effect of particle size on silver leaching rate in oxidation experiment

Particle diameter/μm	Silver recovery/%
160 - 180	22
140 - 160	26
120 - 140	30
100 - 120	37
80 - 100	44
60 - 80	98.12
40 - 60	98.30

3.1.2 Effect of partial oxygen pressure

It is a necessary condition that enough oxygen is used to disintegrate the packing materials of Ag_2S. As shown in Fig. 1, to perform the oxidation process at 80 - 90 ℃ and under oxygen pressure of 10^6 Pa for 5 h is su-

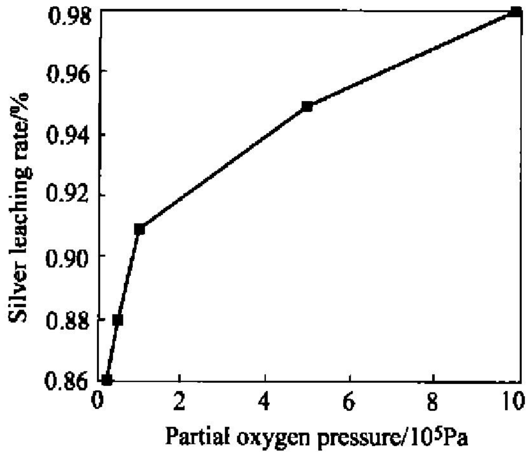

Fig. 1 Effect of partial oxygen pressure on silver leaching rate in oxidation experiment

fficient for thiourea leaching process.

3.1.3 Effect of temperature

It can be seen from Fig. 2 that with increasing temperature, the silver leaching rate is also increased. The optimum decomposition effect of oxidation is obtained at 80 - 90 ℃, where the silver leaching rate is the highest. At the same temperature and different partial oxygen pressure, the silver-leaching rate is different. Therefore, fixing the temperature and increasing the partial oxygen pressure can decrease the oxidation time(the top line).

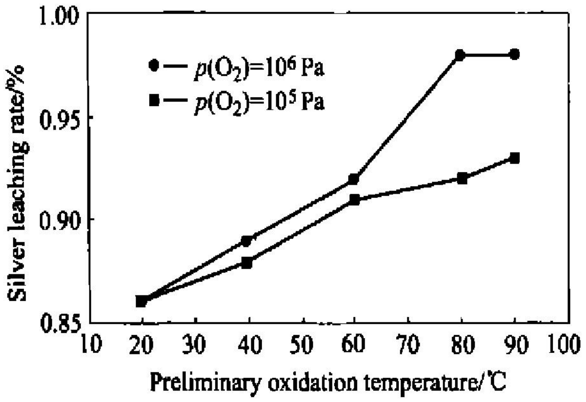

Fig. 2 Effect of temperature in oxidation experiment on silver leaching rate

3.1.4 Effect of oxidation time

From Fig. 3, it is obvious that the silver-leaching rate increases proportionally with the oxidation time. The silver leaching rate reaches the maximum level after 5 h oxidation, which means the preoxidation process is thoroughly performed. Thus, lengthening the oxidation time will do little influence on the silver-leaching rate.

According to above experimental results, the optimum preoxidation conditions are: particle size 40 - 60 μm, partial oxygen pressure 10^6 Pa, temperature 80 - 90 ℃, and oxidation time 5 h. After preoxidation process, the sample particles become small, even and light. Moreover, particles of simple sulfur substance are found in the oxidation experiment.

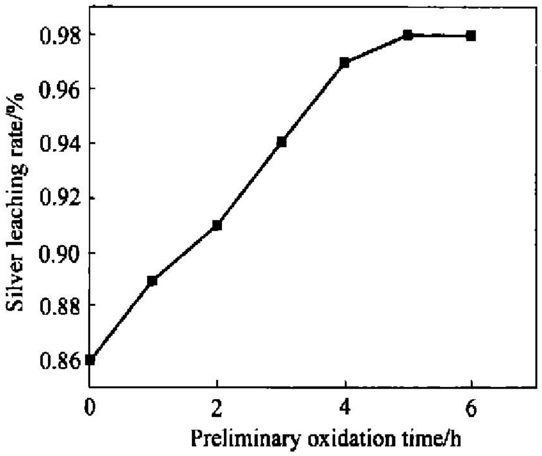

Fig. 3 Effect of time in oxidation experiment on silver leaching rate

3.2 Thiourea leaching

The main influential factors in the thiourea leaching experiment are pulp density, temperature, pH value, ferric ion concentration, stirring velocity, leaching time, thiourea concentration and its consumption. The former five factors have the same changing tendencies as those in the direct thiourea leaching process, which have been studied in large quantities[3-6]. Here, only leaching time, thiourea concentration and its consumption are concerned.

3.2.1 Effect of leaching time

The silver-leaching rate increases with increasing leaching time at the first stage while the other conditions keep unchanged(pH = 2.0 - 2.5, $[Fe^{3+}] \geqslant 0.0159$ mol/L, temperature of 20 - 40 ℃, $\varphi(\text{liquid}):\varphi(\text{solid}) = 10:1$, $\rho(\text{TU}) = 6$ g/L). The leaching rate is higher than 98% after leaching for about 1.5 h at 40 ℃, and it will no longer increase as the leaching time is prolonged.

Therefore, with the preoxidation process on the zinc residues, 1.5 h, which are much shorter than 2 - 3 h of direct silver leaching, will be enough for thiourea silver-leaching. Furthermore, the silver-leaching rate increases with increasing temperature, and will keep constant at 50 ℃ due to the reason that the thiourea is unstable above 50 ℃.

3.2.2 Effect of thiourea mass concentration and consumption

As other parameters keep constant, the preoxidation process on the zinc residues influences the thiourea mass concentration and consumption result. When the thiourea mass concentration is lower than 6 g/L, the silver-leaching rate is not the highest and increases with the thiourea mass concentration increasing, whereas, when the thiourea mass concentration reaches 6 g/L, the silver-leaching rate gets to the highest. The thiourea mass concentration is not the actual consumption of thiourea, so the concentration of the thiourea solution recycled and regenerated from the experiment should keep 6 g/L by adding thiourea continuously. From theoretical calculation, the consumption of the thiourea is 1 032 g/t of hydrometallurgical zinc residues, but in actual experiment, the amount is 1 500 g/t or so, which is consumed by its own oxidization. However, without the process of preoxidation, the actual consumption of thiourea is more than 1 600 g/t, which is larger than the opposite process. In a whole, the preoxidation process can reduce the consumption of thiourea.

4 OXIDATION-LEACHING MECHANISM AND LEACHING KINETICS

4.1 Mechanism of preoxidation thiourea leaching

The molecular formula of thiourea is H_2NCSNH_2, simplified as TU, which is freely soluble and neutral. TU is unstable and easy to decompose in alkali solutions but is stable in acid solutions, and it can form complex compound $[Ag(H_2NCSNH_2)_3]^+$ (abbreviated as $[Ag(TU)_3]^+$, with complexation constant of $10^{13.1}$)[1] with Ag^+. As a result, TU has strong soluble and complex abilities to Ag_2S, AgCl and metal silver etc in the zinc residues.

The reaction of Ag_2S with thiourea in the acid solution containing Fe^{3+} is a kind of typical oxidation-reduction reaction. The solving process can be divided into two steps shown as following equations:

$$Ag_2S + 2Fe^{3+} \rightarrow 2Ag^+ + S^0 + 2Fe^{2+} \tag{1}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{2}$$

$$Ag^+ + 3TU \rightarrow Ag(TU)_3^+ \tag{3}$$

where K_{sp} of Ag_2S is 6.3×10^{-50}. The complexation constant of $Ag(TU)_3^+$ is $10^{13.10}$. So Ag_2S is hard to send out the ion Ag^+ to combine with thiourea without participation of oxidant Fe^{3+} and acids. If the oxidant Fe^{3+} and acids attend the reaction, the result will be $\varphi_{Fe^{3+}/Fe^{2+}} = 0.771$, and $\varphi_{S/Ag_2S} = -0.036\,2$[12]. It is conceivable that Eqn. (1) is easy to happen with sedimentation of simple substance S, and Ag^+ is also easy to combine with thiourea, as shown in Eqn. (3). Above two reactions are considerably slow in respect for Ag_2S is thickly packed by many other sulfides and simple sulfur, which greatly obstructs the acceleration of the mass transferring velocity in the reaction.

The aim of pressurized preoxidation process is to decompose the sulfides, which thickly pack Ag_2S and sulfur, as far as possible to make Ag_2S be re-oxidized to react with halogenides in the minerals to produce silver halides, such as:

$$Ag_2S + X^- + 2Fe^{3+} \rightarrow 2AgX + 2Fe^{2+} + S \tag{4}$$

or

$$Ag_2S + 2X^- + O_2 + 2H_2O \rightarrow 2AgX + 2H^+ + SO_4^{2-} \tag{5}$$

where X represents halogen such as F, Cl and Br. After preoxidation, the silver exists in the form of halogenide in the solids, and in the next thiourea leaching reaction, the naked Ag_2S or silver halides are more easy to combine with thiourea and dissolve in the liquid phase:

$$(AgCl,\ AgBr,\ AgF) + TU \rightarrow Ag(TU)_3^+ + (Cl^-,\ Br^-,\ F^-) \tag{6}$$

In the experiments, the obvious effect of particle size on the silver-leaching rate shows that the bigger particles are more difficult to be oxidized and leached for their serious packing effects. In addition, according to the earlier study of direct thiourea leaching[3-6], the size of large particles will reduce by 10 − 30 μm after the leaching reaction. It indicates that the sulfides packing the silver sulfide are slowly corroded by the oxidant Fe^{3+} and thiourea in the leaching reaction before the silver sulfide reacts with thiourea. Thus the silver-leaching rate is very low and the thiourea consumption is comparatively large in the leaching reaction. Therefore, the leaching process is accordant with the "shrinking core" reacting models[6].

Consequently, the preoxidation process obtains the objective. From the results of preoxidation experiment, the preoxidation process made the sample particles become thinner and lighter, which explained that the packing materials were decomposed. From XRD patterns (as shown in Fig. 4) of the samples after preoxidation, it is obvious that contents of the sulfides such as ZnS, CuS, FeS, PbS and Fe_3O_4 decreased greatly (the abundance ratio is tremendously dropped), and accordingly, large numbers of $PbSO_4$, $CuFe_2S_3$ and simple sulfurs are formed. The appearance of simple sulfur in the sample after preoxidation process shows the preoxidation result, and makes it clear that the sulfur during the pressurized-preoxidation process is not oxidized directly into SO_4^{2-}, but be oxidized by Fe^{3+} into zero valence. As a result, during the whole preoxidation process and thiourea leaching reaction, Fe^{3+} is the direct oxidant on sulfides instead of oxygen.

Moreover, the results of the preoxidation experiments show that the samples after preoxidation process have much better results than the samples without preoxidation process in leaching time, thiourea consumption, leaching rate and whatsoever, as shown in Table 3.

In the earlier study, it concluded that the decision step controlling the whole reaction velocity

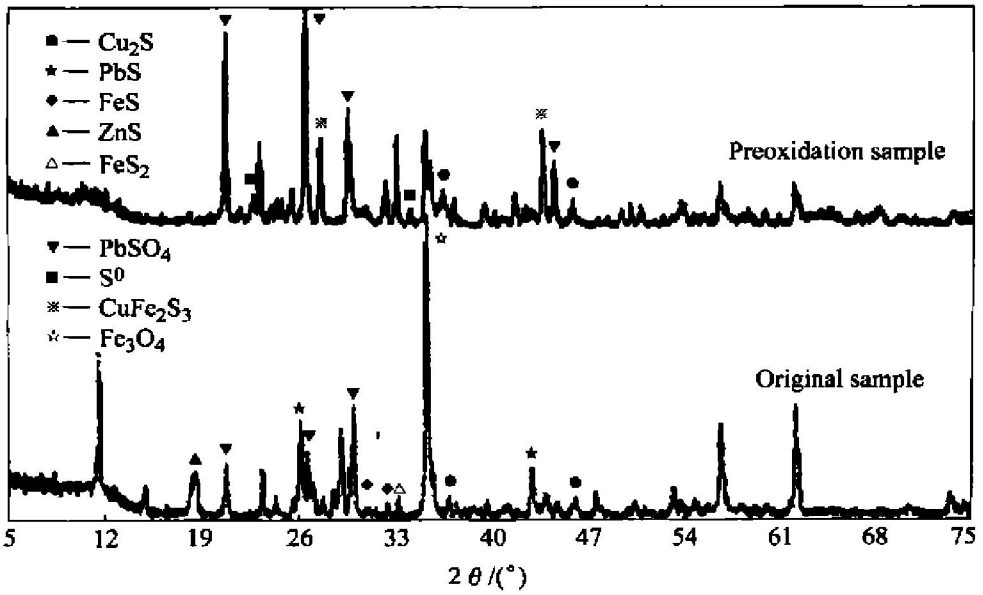

Fig. 4 XRD patterns of original samples and preoxidation samples

Table 3 Contrast of results of leaching experiments with or without preoxidation

Experiment	Time/h	Thiourea consumption/ ($g\cdot t^{-1}$)	Silver leaching rate/%
With preoxidation	1.5	1 500	98.30
Without preoxidation	2	1 600	86.69

was "the solid film diffusion"[6] in the thiourea leaching reaction. The leaching time was shortened after the preoxidation process, which indicated that the solid film turned thinner, and the leaching velocity became faster. The thiourea consumption decreased in the thiourea leaching reaction indicated that the thiourea used to decompose the packing substances around the silver sulfide reduced and so did the oxidization process of thiourea during reaction.

4.2 Leaching kinetics

The "shrinking core" model written as follows can explain the kinetics of the preoxidation process and leaching reaction[6]:

$$1-\frac{2}{3}R-(1-R)^{2/3}=k_e t \tag{7}$$

$$k_e=\frac{8VDC}{\sigma d^2} \tag{8}$$

where R is the silver leaching rate, k_e is diffusion velocity constant, t is leaching time, V is solution volume, D is diffusion coefficient, C is leaching agent concentration, d is particle diameter of the solid phase, σ is reacting system density. The formula clearly expresses the relation between the silver leaching rate and leaching time.

According to this model, k_e should be a constant while the TU concentration(C), particle diameter of the solid(d), and temperature(T) keep unchanged. The relation between the leaching time t and formula $1-(2/3)R-(1-R)^{2/3}$ is shown in Fig. 5 according to the result of experiments. Then, the value of k_e at every temperature can be obtained from Fig. 5. k_e is the function of temperature, which can be described by the Arrhenius equation as follows:

$$k_e=A\exp(-E/RT) \tag{9}$$

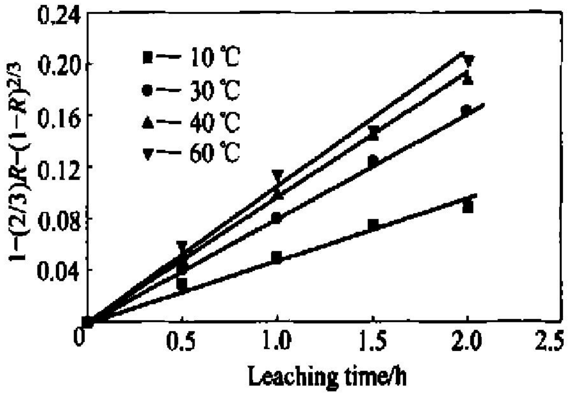

Fig. 5 Relation between leaching time and formula

The Arrhenius linear plot shown in Fig. 6 can be obtained by k_e at different temperature and reciprocal value of temperature $1/T$. The plot is a straight line with slope of -0.6619×10^3. Calculated by the Arrhenius equation, the activation energy of the diffusing process is 12.68 kJ/mol, which is a little lower than the activation energy (13.26 kJ/mol) from the direct thiourea silver leaching[6].

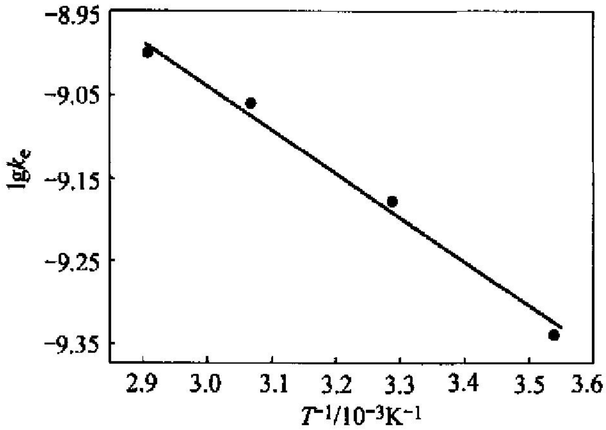

Fig. 6 Arrhenius plot for leaching experiments

5 CONCLUSIONS

1) As for the leaching-resistant zinc residues, over 98% silver leaching rate can be obtained through the process of pressurized preoxidation and thiourea leaching. The optimum preoxidation conditions are: particle size range 40 - 60 μm, oxygen partial pressure 10^6 Pa, temperature 80 - 90 ℃, pH = 1.0, and leaching time 5 h. The preoxidation process reduces the silver leaching time and the thiourea consumption.

2) The optimum conditions of thiourea leaching are: $\rho(\text{TU}) = 6$ g/L, temperature 40 ℃, pH = 2.0 - 2.5, $[\text{Fe}^{3+}] \geq 0.0159$ mol/L, leaching time 1.5 h.

3) The kinetics of the leaching reaction is accordant with the "shrinking core" model. The decision step controlling the whole reaction velocity is the "solid film diffusion" in the thiourea leaching reaction. Furthermore, the reaction activation energy is 12.68 kJ/mol.

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