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Scientific Paper

INDUSTRIAL PRECIPITATION OF CUPRIC HYDROXY-SALTS

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Abstract

The reaction between $Cu_2Cl(OH)_3$ and slaked lime suspension was studied. It was found that the concentrations of the participating ions in the reaction mixture determined which of the possible products CuO, or $CaCu_3Cl_2(OH)_6$, or $CaCu_4Cl_2(OH)_8$ was precipitated. The reaction conditions also influenced the repose times of the precipitates. The considerably longer repose time of CuO than that of the MB4 enables industrial production of the MB4 of the prescribed purity. When co-precipitation of MB4 and CuO occurs, it causes blackening of the product. From the composition and the concentrations of all the ionic species present in equilibrium with the solid phase, the solubility products of the precipitated compounds were estimated.

Key words: Copper fungicides, copper oxide, calcium tri-copper di-chloride hexa-hydroxide, calcium tetra-copper di-chloride octa-hydroxide, solubility constant, industrial precipitation.

Introduction

Copper based fungicides still play an important role in plant protection, irrespective of the many new organic substances which constantly appear on the market. The reason is the over hundred year tradition[1] and favorable application experience, especially that related to their relatively low toxicity for mammals. The efficiency of copper fungicide depends on its ability to produce a lethal concentration of copper(II) ions before the growth of fungi can take place, and which at the same time, does not exceed the phytotoxic concentration limit. In order to enable the protection of many different plant species against various possible fungal diseases, different kinds of special copper substances must be used.

Mixing a copper(II)oxychloride ($Cu_2Cl(OH_3)$, written in some literature as $CuCl_2{\cdot}3Cu(OH)_2$), suspension with slaked lime is an important industrial process for the production of some highly efficient special copper fungicides.[2] The reaction of copper(II)oxychloride with lime may give three different chemical substances: copper oxide (CuO), and two calcium copper chloride hydroxides: calcium tri-copper di-chloride hexa-hydroxide and calcium tetra-copper di-chloride octa-hydroxide, with chemical formulae $CaCu_3Cl_2(OH)_6$ and $CaCu_4Cl_2(OH)_8$. In some literature sources these chemical formulae can be found written as $CaCl_2{\cdot}3Cu(OH)_2$, and $CaCl_2{\cdot}4Cu(OH)_2$, respectively. Their commercial names, used by the producer, are MB3 and MB4, respectively. MB4 represents the main active ingredient in a high quality commercial fungicide, Cuprablau-Z, which is produced by Cinkarna Celje.

Previous work. The precipitation of some basic copper complexes from sulfate and nitrate solutions was studied by McFadyen and Matijević.[3] The goal of their research was the determination of the equilibrium conditions for ageing of solutions containing copper(II) nitrate and copper(II)sulfate. No special attention was paid to kinetics and other parameters important in the industrial production of those compounds, except for the mean diameter of the precipitated particles. The equilibrium concentration of copper ions was measured by atomic absorption spectrometry and a laboratory made ion selective electrode with a reproducible linear response in the range from $5{\cdot}10^{-6}$ to 10^{-1} mol/L. The precipitation of copper oxide - tenorite - was studied by Barthon and Bethke[4], Nasanen and Tamminen[5] and some other authors.[6] Barthon and Bethke estimated the solubility product of copper(III) oxide using a technique similar to ours. Their result, $K_{SP}=10^{-19.7}$, which is based on two separate experiments, originated from reaction of atacamite (copper(II)oxychloride) and brochanite (copper basic sulfate) with OH^-, and is in a good agreement with other cited studies.[4-6]

Erdös et al.[7] studied the thermochemical, crystallographic and infrared-spectrometric properties of calciumcopperchloride hydrates. The product, $4Cu(OH)_2{\cdot}CaCl_2{\cdot}3.5\ H_2O$, formed when copper was immersed in a solution of $CuCl_2$, and oxidized with oxygen, is equivalent to our MB4. On heating up to 215 °C, the authors observed the formation of a mixture of CuO and $2Cu(OH)_2{\cdot}CuO{\cdot}CaCl_2{\cdot}H_2O$. This compound relates to our MB3.

The objectives of the present study. The main stimulation for our research was the unstable quality of Cuprablau-Z fungicide, which was most probably due to the fact that the active copper substance was often not pure enough to ensure its optimal fungicidal efficiency. During the precipitation of MB4 in an industrial reactor, via the reaction between copper(II)oxychloride and slaked lime, the conditions must be controlled within a very narrow range in order to prevent formation of undesired by-products. A particularly unwanted side reaction is the formation of copper oxide. Its appearance in MB4 can be easily observed, because of the blackening of the product. While the exact mechanisms of the related reactions are not completely known, the aim of this work was to carry out the relevant experiments, which would enable us, at least on a practical level, to recognize the conditions under which the preferred product is formed.

Theoretical basis

When the Cu^{2+}, Ca^{2+}, OH^- and Cl^- ions are simultaneously present in an aqueous solution, any of the four substances copper oxychloride, MB4, MB3 or copper oxide may start to precipitate, depending on the relative concentrations of the four ions. In the present investigation, however, different concentration levels of the free ions in a suspension were achieved by varying the relative amounts of the reactants copper chloride, calcium hydroxide, or copper(II)oxychloride and calcium chloride, and temperature. If the ionic product of any of the above mentioned chemical substances exceeds its solubility product, the initial condition for precipitation is met, and precipitation may begin. The start of the precipitation reaction may be delayed for a certain time, called the induction time. In the system under examination, in some cases induction times as long as several days were encountered.

The process of conversion of a copper(II)oxychloride suspension is assumed to proceed in three stages, (1-3):

1. The dissolution of copper(2)oxychloride:

$$Cu_2Cl(OH)_3 \Leftrightarrow 2Cu^{2+} + Cl^- + 3OH^- \tag{1}$$

and slaked lime:

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^- \tag{2}$$

2. The transport of the dissolved ions through the solution phase from the surface of $Ca(OH)_2$ particles to the point where the target compound is formed, and

3. The precipitation of the sparingly soluble compound (a, b, or c):

a) copper oxide:

$$Cu^{2+} + 2OH^{-} \Leftrightarrow CuO + H_2O \tag{3}$$

b) MB3:

$$4Ca(OH)_2 + 6Cu_2Cl(OH)_3 + CaCl_2 \Leftrightarrow 4CaCu_3Cl_2(OH)_6 \tag{4}$$

c) MB4:

$$2Cu_2Cl(OH)_3 + Ca(OH)_2 \Leftrightarrow CaCu_4Cl_2(OH)_8 \tag{5}$$

Two of the reactants ($Cu_2Cl(OH)_3$ and lime) and all the products are solids, and with the exception of slaked lime, all sparingly soluble. The thermodynamic solubility products of these compounds can be defined as:

$$K_{SP\,oks} = a^{*2}_{Cu^{2+}} \cdot a^{*}_{Cl^{-}} \cdot a^{*3}_{OH^{-}} \cdot \tag{6}$$

for copper(2)oxychloride,

$$K_{SP\,lime} = a^{*}_{Ca^{2+}} \cdot a^{*2}_{OH^{-}} \tag{7}$$

for slaked lime,

$$K_{SP\,CuO} = a^{*}_{Cu^{2+}} \cdot a^{*2}_{OH^{-}} \tag{8}$$

for copper oxide,

$$K_{SP\,MB\,3} = a^{*}_{Ca^{2+}} \cdot a^{*3}_{Cu^{2+}} \cdot a^{*2}_{Cl^{-}} \cdot a^{*6}_{OH^{-}} \tag{9}$$

for MB3 and

$$K_{SP\,MB\,4} = a^{*}_{Ca^{2+}} \cdot a^{*4}_{Cu^{2+}} \cdot a^{*2}_{Cl^{-}} \cdot a^{*8}_{OH^{-}} \tag{10}$$

for MB4.

The activity a_i of an ionic species i is related to its concentration C_i by

$$a_i = \gamma_i \cdot \frac{C_i}{C^{o}{}_{i}} \tag{11}$$

where $C_i^o = 1\ mol/L$ (related to the hypothetical state) and γ_i is the activity coefficient. The activity coefficients were obtained from the extended Debye- Hückel equation[8]

$$\ln \gamma_i = -\frac{A}{\left(1 + r_i B \sqrt{I}\right)} \cdot z_i^2 \sqrt{I} \tag{12}$$

where A and B are the Debye-Hückel parameters, z_i the ion charge and r_i the ion-size parameter. The values of A and B vary with temperature and dielectric constant of the solvent. The values for the constants A, B at a given experimental temperature were taken from Table 8.3 in Dean.[9] I is the ionic strength of the medium, defined as:

$$I = 0.5 \sum_i C_i \cdot z_i^2 \tag{13}$$

Precipitation is a complex process and can be further divided into nucleation, crystal growth and possible secondary changes. The size distribution of the precipitated particles essentially depends on the number of initially formed nuclei, which in turn depends on the supersaturation of the solution. The relative supersaturation is defined by[10]

$$S = \frac{K_{IP} - K_{SP}}{K_{SP}} \tag{14}$$

where K_{IP} is the thermodynamic ionic product defined by the product of activities of the corresponding ions, i

$$K_{IP} = \prod_i a_i^{\nu_i} \tag{15}$$

It is commonly observed that higher supersaturation leads to smaller particle sizes. Data for the solubility constants are therefore needed to be able to find conditions under which the desired chemically pure compound is produced. Since the solubility constants of the copper complexes we are dealing with are not available, or are very scarce, we have made our own estimates of their values. There are quite a few different methods for experimental determination of solubility products; however, none of them is generally applicable. The main problem in determining the solubility product of a sparingly soluble compound is how to determine the very low activities of the ions present.[11] In some cases, like the dissolution of copper(II)oxychloride, the activity of only one of the ionic species can be determined, while the activities of all other ionic species in the solution have to be calculated from the mass balance rule, taking the relevant ion activity coefficient data[12] into account. This method was recently applied for determining the copper(II)oxychloride solubility product.[13,14] The same method was also applied in the present investigation for determining the solubility constants and the ionic products of copper oxide, MB3 and MB4.

Experimental

Chemicals. In all the experiments, distilled water, pure copper(II)oxychloride prepared by a procedure described elsewhere,[13] and Merck analytical grade calcium hydroxide were used. Chemical,[14] X-ray diffraction and electron diffraction analyses of the products confirmed their chemical composition and purity.

Precipitation experiments. All precipitation experiments were carried out in a thermostatted 10 L container (beaker with double jacket), equipped with a propeller stirrer, a glass tube for purging nitrogen gas through the solution, and a thermometer. The pH of the solution was measured at intervals using a Radiometer glass and reference electrode with a double KCl/KNO_3 junction, and a Radiometer pH-meter, type PH95. The pH meter was standardized against Radiometer® Phthalate buffer (part no. 943-111), and Radiometer® Phosphate buffer (part no. 943-112), respectively, and a precision of +/- 0.01 pH units was achieved. During restoration of equilibrium the solution was purged with nitrogen to remove any possible dissolved CO_2. The temperature of the solution was controlled within +/- 0.1 ^{o}C by an IKA thermostat.

Results and discussion

When sparingly soluble copper(II)oxychloride is mixed with a suspension of slaked lime, three different reactions (3-5) are possible between the dissolved ions giving sparingly soluble precipitates (CuO, or $CaCu_3Cl_2(OH)_6$, or $CaCu_4Cl_2(OH)_8$). To find at which specific process conditions only the preferred copper compound is precipitated, a series of controlled experiments was performed, as is described below. The dissolution of copper(2)oxychloride was carried out in solutions having just the temperature, and the Ca^{2+}, Cl^- and OH^- ion activities required for precipitation of the desired copper compound. A series of experiments was performed to verify the predicted conditions for precipitation of copper(II)oxide, (Experiments No.:1-8), MB3 (Experiment No.:9) and MB4 (Experiment No.:10). The influence of the initial Cl^- ion concentration, (Experiments No.:2,3,4,8), temperature, (Experiments No.:1,2) and the presence of seeds on copper(2)oxide precipitation, (Experiments No.:5,7) were also studied. At the end of each experiment, the solution composition was determined and the product analyzed for purity. From these data, the solubility constants were obtained.

The initial concentrations of the participating ions in the reaction mixture were adjusted to the value at which the desired product is formed, with the aid of copper(2)oxychloride, lime (and calcium chloride, $CaNO_3$, NaCl). The values of the initial ion concentrations in the mixture were taken from the recipes for an industrial process, see Table I.

Table I. Initial parameters in the precipitation experiments.

Exp. No.:	V [L]	$m_{(oxi)}$ [g]	T [^{0}C]	C_{CaCl2} [mol/L]	$C_{Ca(NO3)2}$ [mol/L]	C_{NaCl} [mol/L]	$C_{Ca(OH)2}$ [mmol/L]
1	4.0	5.0	25	-	-	-	1.460
2	4.3	5.0	40	-	-	-	1.300
3	6.0	5.0	40	0.001	0.10		0.976
4	6.3	5.0	40	-	-	0.1	0.929
5	6.3	5.0	40	0.010	0.10		0.929
6	6.3	5.0	40	-	-	-	0.929
7	6.3	5.0	40	0.010	0.10	-	0.929
8	6.3	5.0	40	0.100	-	-	1.390
9	6.3	20.0	40	0.200	-	-	3.310
10	6.3	20.0	40	0.005	0.15	-	4.160

The time dependence of the change of OH^- ion concentration during the precipitation (conversion of copper(II) oxychloride and slaked lime) experiments is presented in Figures 1, 3-5. In Figure 1 the OH^- ion concentration during Experiments Nos.: 2, 9 and 10, where the final products were the pure compounds CuO, MB3 and MB4, is presented. The fastest is the conversion into CuO, slightly slower is the conversion to MB4, whereas conversion into MB3 is a very slow reaction.

Precipitation of CuO. In those experiments where copper oxide precipitates, a higher supersaturation is reflected in a smaller particle size. SEM images, (cf. Figure 2), and XRD analyses show that copper oxide precipitates on the surface of copper(II)oxychloride particles in the form of small lamellae, with an approximate thickness of one tenth of the particle diameter. We were not able to obtain an exact correlation between the supersaturation ratio and the mean particle size in our study, but it can be seen that ordinarily smaller particles precipitate, when the supersaturartion is high. The approximate mean size of the particles varied from half a micron in Experiment No. 2, to over a micron in Experiment No. 4.

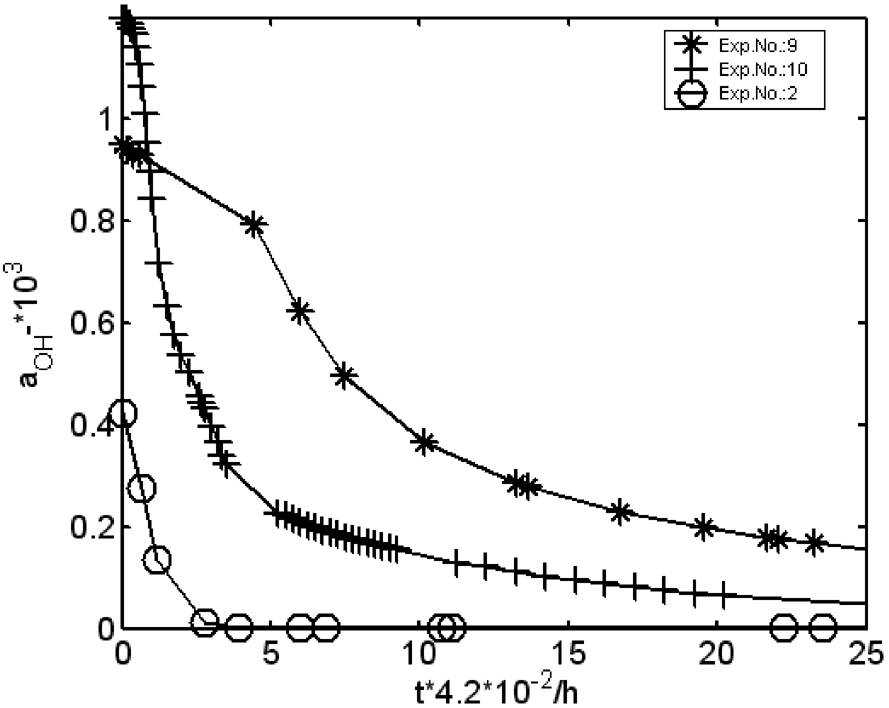

Figure 1. OH- ion activity during the experiments No. 2, 9 and 10, where the final products were CuO, (line o), MB4, (line +), and MB3** (line *). **The scale of the time axis in the case of MB3 is reduced by a factor 5.

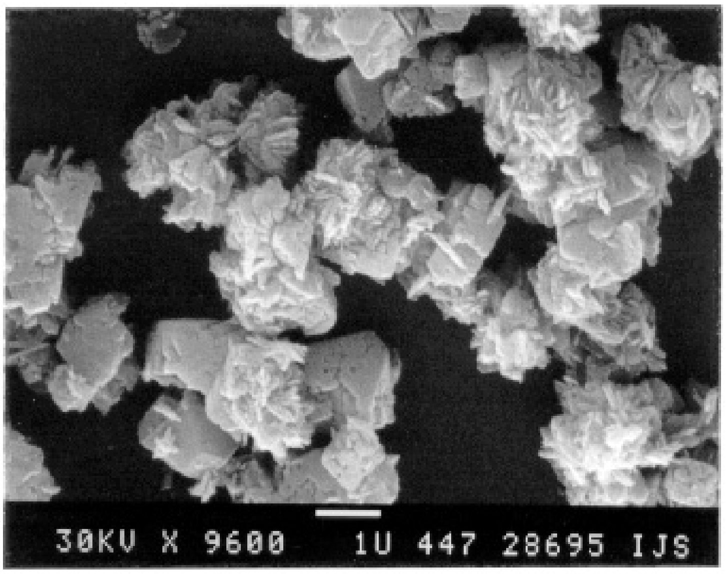

Figure 2. SEM photograph of the CuO tiny crystals growing on the surface of larger copper(II)oxychloride particles, obtained in Experiment No.:2. (The magnification is 9600). The length of the white bar above the image labels represents 1μm.

Precipitation of copper oxide (and the other studied compounds MB3 and MB4 as well) consists of three consecutive steps. The first step is the surface dissolution of copper(II)oxychloride particles into Cu^{2+}, Cl^- and OH^- ions, followed by the transport of ions from the copper(II)oxychloride surface into the bulk of the solution, and finally, the formation of copper oxide nuclei in places where its solubility product is exceeded. In general, any of the three processes could be rate limiting. However, by comparing the experimental rates of copper oxide production in Experiment No. 2, with the estimated maximum rate of copper(II)oxychloride dissolution (Eq. 4), we can easily exclude the dissolution of copper(II)oxychloride as the rate limiting process. The fact that particles of copper oxide grow from the copper(II)oxychloride surface, favors diffusion of ions through the stagnant film of the liquid phase around particles, as the rate limiting process. Using a rough estimate[13,14] of the ion transport rates, based on Newman's[15] theory valid for mixed electrolytes, we found that the Cu^{2+} ion concentration gradient is much too small to ensure the rate of conversion observed in Experiment No. 2. This phenomenon could be explained by intermediate copper complex formation (10).

This hypothesis seems to be supported by the observation that the conversion of copper(II)oxychloride to copper oxide is a temperature dependent process, as can be seen from Figure 3.

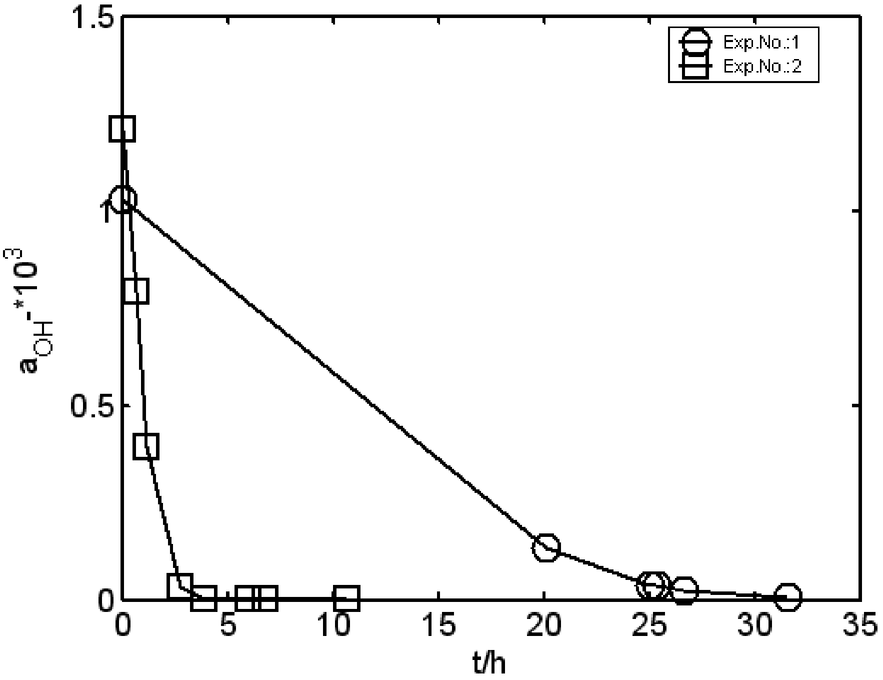

Figure 3. Influence of temperature on the OH- activity during the conversion of copper(II)oxychloride and lime into CuO. Circles: temperature 25 °C; squares: temperature 40 °C.

At the low supersaturation level with respect to CuO applied in Experiment No. 5, a rather long repose time of CuO was observed. A long repose time is probably a consequence of the absence of stable nuclei in the solution. In Experiment No. 7, where the ionic product was only several ten times higher than the solubility product of copper oxide, the supersaturated solution remained stable for 11 days. However, this time could easily be shortened by the addition of copper oxide seeds, as is clearly seen from the curves (a and b) in Figure 4. The repose times of CuO and MB4 are the key parameters in the industrial production of MB4. Because of the rather long repose time of CuO for instance, industrial production of MB4 is possible. In this case, CuO begins to precipitate after most of the MB4 is already formed.

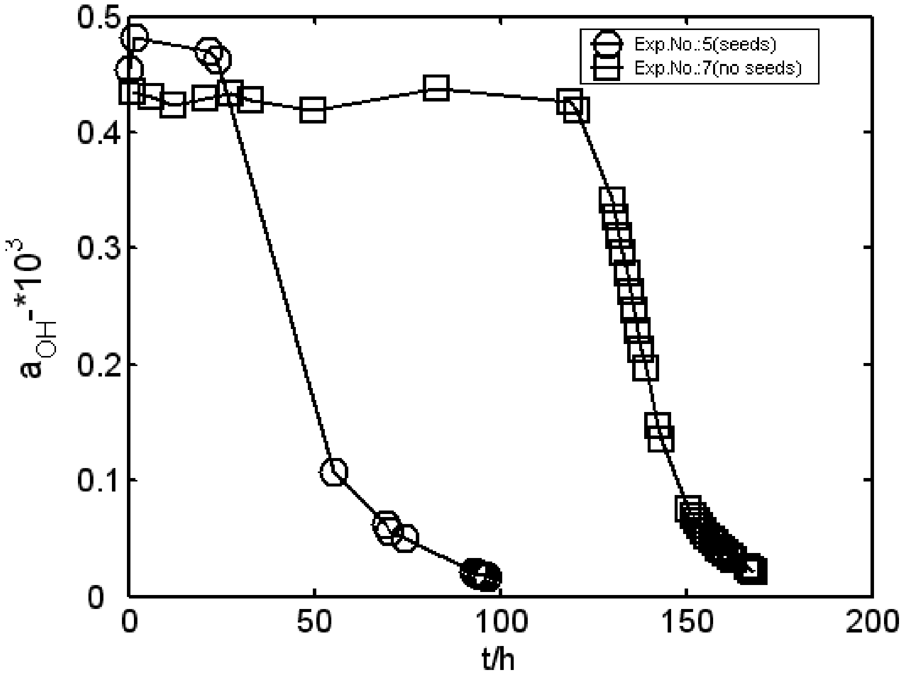

Figure 4. Influence of seeds on the OH- activity during the conversion of copper(II)oxychloride and lime into CuO. Note the legend in the Figure.

From Figure 5 it may be seen that an increase of the initial concentration of Cl^- ions reduces the rate of copper oxide precipitation. This can be explained by the consequent decrease of the concentration of Cu^{2+} ions at the particle surface, which is a consequence of the mass action law, described by Eq.6.

Precipitation of MB3. In Experiment No. 9 the initial concentration of calcium chloride was high enough to precipitate MB3. The rate of reaction was very slow, and after 20 days equilibrium was still not reached. For technical reasons the experiment was stopped at that point. The precipitated particles of the product were relatively large, up to 5 microns in diameter, and regularly shaped, as can be seen from Figure 6.

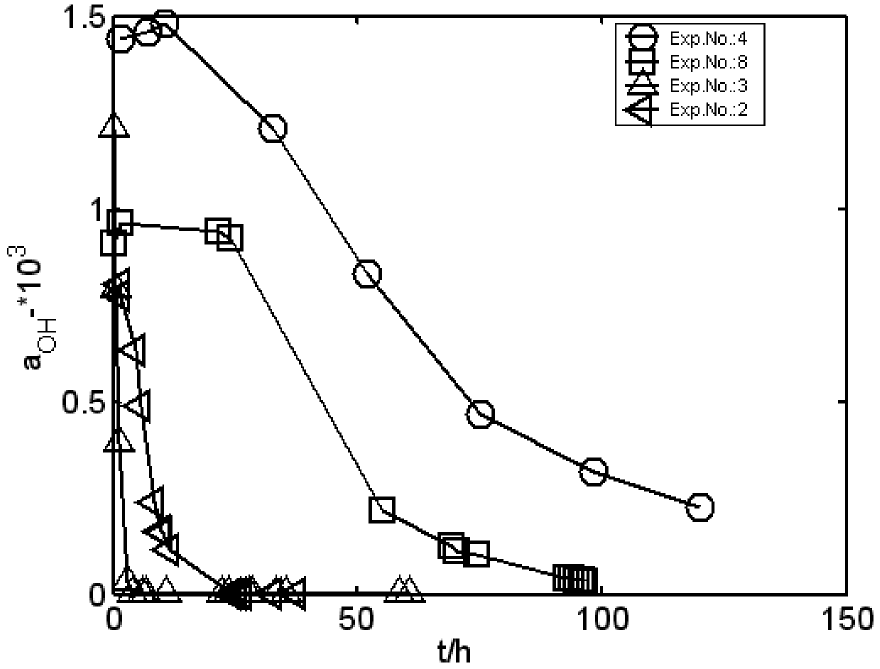

Figure 5. Effect of the Cl^- ion concentration on the OH^- activity during the conversion of copper(II)oxychloride and lime into CuO. The values of the Cl^- concentrations are 0, 0.002, 0.02 and 0.1 mol/L from the left to the right curves.(See Table I.)

The particles grow from the solution side, which suggests that diffusion is not the rate determining process. However, the kinetics of MB3 precipitation seems to be rather complex and an attempt to explain them in detail will be published separately.

Precipitation of MB4. The initial conditions for the experiment No. 10 (ion concentrations) were set in accordance with our industrial experience. The reaction was relatively quick and a characteristic blue colour of MB4 was observed after a few tens of minutes, and remained for the next few hours. But, overnight, the blue colour of the product turned to black, due to the formation of copper oxide. After analyzing the basis of this phenomenon, we found that the basic conditions for formation of copper oxide were fulfilled from the very beginning of the experiment. The delayed appearance of

CuO was then certainly a consequence of the quite long repose time of CuO in this system. This could also explain the blackening of the product in the industrial production of MB4.

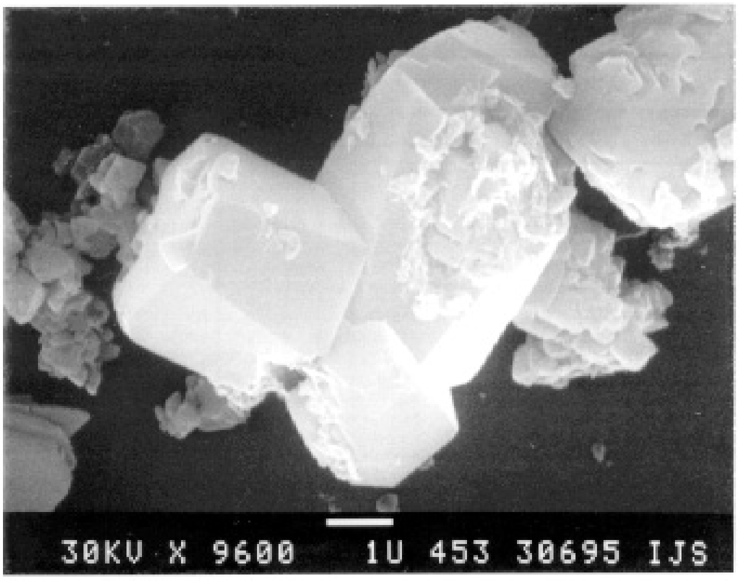

Figure 6. SEM photograph of MB3 crystals obtained in Experiment No.:9. (The magnification is 9600).

As mentioned above, the conversion of copper(II)oxychloride as MB4 was followed by the formation of copper oxide, and hence it was not possible to determine the rate controlling parameters of the reaction. Nevertheless, we can conclude that this reaction is much faster than the conversion of copper(II)oxychloride to MB3 or even to copper oxide. If we want to assure the formation of pure MB4, than according to Eq. 8 and 9, the following condition must be met:

$$\frac{K_{SPMB\,4}}{K_{SPCuO}^{4}} \langle a_{Ca^{2+}} \cdot a_{Cl^{-}}^{2} \qquad (16)$$

In the experiment No. 10, the activity of Ca^{2+} was nearly constant, with an estimated value of 0.028 according to Bromley's method.[11] The activity of Cl^{-} ions at the start of the experiment was estimated as 0.0073, and as 0.013 at the end. It is obvious that during Experiment No. 10 the condition (15) was not met at any time. But, MB4 appeared, (which can be easily observed since it has a clear blue colour) because of the smaller repose time of the precipitated MB4 than of CuO, as is clearly seen in Figure 6. A comparison with Experiment No. 3, where the supersaturation of Cu^{2+} and

OH^- ions was about 100 times K_{SP}, shows that in the first 2 hours no visually observable darkening occurred.

Let us now review the conditions under which the conversion of copper(II)oxychloride to MB4 takes place in a real industrial process. In this case, if the presence of pure copper(II)oxychloride and slaked lime is assumed, the estimated supersaturation of the solution with respect to Cu^{2+} and OH^- ions is about 10^6 times larger than the solubility product of copper oxide. At the same time, however, the supersaturation with regard to MB4 is only a few orders of magnitude higher, so the production of pure MB4 is not likely under such conditions. As a matter of fact, it is unusual for MB4 to precipitate, at all. The fact that under such conditions industrial production is possible is probably due to the presence of impurities. Due to the nature of the copper(II)oxychloride industrial production process, Cl^- ions cannot be removed completely from the surface of the solid particles. It can easily be shown that the presence of Cl^- ions in concentrations as low as 0.01 mol/L can lower the supersaturation of the solution with respect to Cu^{2+} and OH^- ions, so that the solubility product of copper oxide is exceeded only by a factor 100 or so, which, according to our experimental experience, is sufficiently low to ensure industrial production of MB4.

As a matter of fact, the solubility product of MB4 is equal to the product of the solubility constants of MB3 and CuO, as follows:

$$K_{SP\,MB4} = K_{SP\,MB3} \cdot K_{SP\,CuO} \tag{17}$$

If we wish to precipitate pure MB4 without the co-precipitation of any amount of MB3, two conditions must be achieved: $K_{IP\,MB3} < K_{SP\,MB3}$ and $K_{IP\,MB4} > K_{SP\,MB4}$. This can only be met if $K_{IP\,CuO}$ is higher than $1.4.10^{-19}$, which exceeds the estimated value of the copper oxide solubility product. From this reality, we can conclude that it is impossible to precipitate chemically pure MB4 without simultaneously precipitating at least some amount of either copper oxide or MB3. It is important to note that in all the precipitation experiments, copper(II) oxychloride was used for attaining the required ionic conditions.

Estimation of the solubility constants. The products of reactions (3) and (4) are sparingly soluble in water. Because of the extremely low value of the solubility constants of the precipitates, the activities of all but one free ionic species in solution are too low to be determined separately. The exception is the OH^- ion concentration, the activity of which is accessible through measurements of the pH of the solution. From the experimental pH values the activities of the OH^- ions were determined using the relation

$$a_{OH^-} = \frac{K_W}{10^{-pH}} \tag{18}$$

The concentrations of all other ionic species can be estimated from the stoichiometry of the precipitation reaction. The details of the method applied are described elsewhere.[4,11,13]

In the case where the reaction product is copper oxide, the final concentration of Cl^- ions is equal to

$$C_{Cl^-} = C^0_{Cl^-} + C^0_{OH^-} + C_{OH^-} \tag{19}$$

Here, $C^0_{Cl^-}$ and $C^0_{OH^-}$ are the initial concentrations of Cl^- and OH^- ions, respectively, and C_{OH^-} is the final concentration of OH^- ions.

From the pH value of the solution after 60 hours, when the equilibrium state was reached, we obtained the equilibrium OH^- ion concentration. Using Equations 6 and 11-13, we estimated the solubility product of copper oxide (Eq. 8). In the same way the solubility products of both basic copper chloride salts were determined. When the product is MB3, the final concentrations of Cl^- and Ca^{2+} are related to:[13]

$$C_{Cl^-} = C^0_{Cl^-} - \frac{1}{3}\left(C^0_{OH^-} - C_{OH^-}\right) \tag{20}$$

and

$$C_{Ca^{2+}} = C^0_{Ca^{2+}} - \frac{2}{3}\left(C^0_{OH^-} - C_{OH^-}\right) \tag{21}$$

When MB4 precipitates, the extra calcium chloride is not needed at the beginning of the process (cf. Eq. 5). The change in the concentration of chloride ions is a result of simultaneous copper(II)oxychloride dissolution and MB4 precipitation. The molar ratio of Cl^- and Cu^{2+} ions is equal in both compounds $Cu_2Cl(OH)_3$ and $CaCu_4C_{l2}(OH)_8$, which preserves the constant ratio of concentrations of both ionic species in the solution. The Ca^{2+} concentration changes to:

$$C_{Ca^{2+}} = C^{0}_{Ca^{2+}} - \frac{1}{2}\left(C^{0}_{OH^{-}} - C_{OH^{-}}\right) \tag{22}$$

The solubility product of copper oxide. In Experiment No.:2, copper(II)oxychloride and copper oxide were the only two precipitated compounds, and an equilibrium with dissolved Cu^{2+}, Cl^{-} and OH^{-} ions can be assumed. No other ions, except for a small quantity of Ca^{2+} ions, are present. The ionic strength during the experiment was kept at 0.0039. The copper oxide solubility product in solution was estimated at $5.6 \cdot 10^{-20}$, which is in a good accord with the value of Barton and Bethke ($4.6 \cdot 10^{-20}$).[4]

The solubility product of MB4. Due to the extremely low value of the solubility product of MB4, it was possible to estimate only its lower and upper limits. From the fact that the only product of the experiment No. 9 was MB3, the lower limit of K_{SP} can be set at $1.18.10^{-78}$. On the other hand, the fact that at the beginning of Experiment No. 10 MB4 was precipitated gives the upper limit for K_{SP} of $8.4.10^{-76}$.

The solubility product of MB3. A rough estimate of the solubility product was obtained from the state of solution, i.e., the concentrations of Cu^{2+}, Ca^{2+}, Cl^{-} and OH^{-} ions. The activity coefficients were estimated using Bromley's expression 11, since the ionic strength was about 0.6 mol/L. The estimated value ($8.3.10^{-60}$) is at the upper limit of the MB3 solubility product. The literature value is slightly lower.[16,17] However, the result obtained was considered accurate enough for further engineering applications.

Conclusions

The reaction between copper(II)oxychloride and slaked lime in suspension was studied at different process conditions. This reaction may give three different chemical substances: copper oxide, and two calcium copper chloride hydroxides: MB3 and MB4. The investigation i) provided data for the process conditions that must be achieved in industrial precipitation of the copper, calcium basic salts, MB4 and MB3, of stable quality; and ii) helped to elucidate some phenomena that occasionally take place in an industrial reactor.

The most important findings are:

- CuO: The presence of seeds, elevated temperature and a high Cl^- ion concentration considerably increase the rate of CuO precipitation.

- MB3: Industrial production of MB3 is possible only when excess calcium chloride is present in a suspension of copper(II)oxychloride and slaked lime. The presence of Cl^- ions in the concentration range from 0.001 to 0.1 mol/L has two beneficial effects; it raises the ionic product of MB3, and simultaneously reduces the concentration of Cu^{2+} ions in the solution and consequently the ionic product of CuO, which reduces the possibility for its co-precipitation with MB3.

- MB4: In the industrial production of MB4, the operating conditions are such that the solution is supersaturated with respect to both MB4 and CuO, and hypothetically, the simultaneous precipitation of both compounds is possible. However, because of the shorter repose time of MB4 in comparison with the repose time of copper oxide, CuO begins to precipitate after MB4 precipitation has already ceased. The undesired co-precipitation of CuO causes the blackening of the product.

The thermodynamic solubility products of all three precipitated compounds, determined by the Bromley's method[10] are presented in Table 2.

Table 2. Thermodynamic solubility constants of basic copper salts at 40 °C.

Compound	K_{sp}	Uncertainty (%)
CuO	$5.6.\ 10^{-20}$	± 10
MB3	$8.3.10^{-60} – 1.10^{-58}$	± 10
MB4	$1.2.10^{-78} – 8.4.10^{-76}$	± 10

Finally, this work led to interesting practical results, which were beneficially implemented in the process of production of Cuprablau-Z fungicide at the Cinkarna Celje plant.

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Nomenclature

a_i	Activity of species *i* in the solution(i ={Cu^{2+}, Cl^-, Ca^{2+}, OH^-}); [/]
C_i	Concentration of species *i* (i ={Cu^{2+}, Cl^-, Ca^{2+}, OH^-}); mol/L
K_{IPj}	Ionic product of component *j* ({*j*= CuO, oxi, MB3, MB4, lime})
K_{SPj}	Thermodynamic solubility product of *j*
S_j	Supersaturation ratio of *j*
ν_ι	Stoichiometric number of *i*
*	Equilibrium value
lime	Calcium hydroxide , $Ca(OH)_2$
MB3	calcium tri-copper di-chloride hexa-hydroxide with the chemical formula $CaCu_3Cl_2(OH)_6$
MB4	calcium tetra-copper di-chloride octa-hydroxide with the chemical formula $CaCu_4Cl_2(OH)_8$
oks	di-copper chloride tri-hydroxide or Copper(2)oxychloride with the chemical formula $Cu_2Cl(OH)_3$.

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Povzetek

Industrijsko pridobivanje težkotopnih bakrovih kompleksov temelji na reakciji med bakrovim (2) oksikloridom in gašenim apnom. Reakcija poteka v suspenziji in lahko vodi do treh različnih čistih produktov, ali do njihovih zmesi. Pričujoči prispevek obravnava vpliv procesnih spremenljivk, kot so začetna sestava reakcijske zmesi, temperatura in dodatek kali, na potek precipitacije CuO, MB3 in MB4. Eksperimenti kažejo, da poteka preobarjanje različnih soli različno hitro in po različnih mehanizmih. Na osnovi te raziskave je bila opravljena optimizacija procesa pridobivanja fungicida Cuprablau-Z v tovarni Cinkarna Celje.