New Low-Temperature Technology of Producing Calcium Feed Phosphate with Microelements

Józef Hoffmann
Department of Chemistry, Institute of Inorganic Technology and Mineral Fertilizers, Technical University of Wrocław, 50 370 Wrocław, wyb. Stanisława Wyspiańskiego 27, Poland

**Abstract:** The possibility of producing feed calcium phosphates in a way ensuring a low physical water content in the product was investigated in laboratory conditions. For this purpose the process use of a phosphoric acid solution with a higher (than in conventional methods) P$_2$O$_5$ content (53-63% by wt. P$_2$O$_5$) with CaO (molar fraction of 0.5-0.8) and CaCO$_3$ in the phosphoric acid neutralizing mixture was tested. Phosphates with a high content of phosphorous forms highly assimilable by animals, soluble in 0.4% HCl (94-99%), were obtained. The physical water content of 1-4% by wt. H$_2$O was obtained when a phosphoric acid solution with a 59% by wt. P$_2$O$_5$ content and a CaO molar fraction of 0.8 in the neutralizing mixture were used and for a phosphoric acid solution with a 63% by wt. P$_2$O$_5$ content. A temperature above 160°C was obtained when respectively phosphoric acid with a 59% by wt. P$_2$O$_5$ content and the highest CaO fraction in the neutralizing mixture and a phosphoric acid solution with a 63% by wt. P$_2$O$_5$ content were used. An elevated CO$_2$ content in the products, indicating an increase in the unreacted calcium carbonate content, was found when a phosphoric acid solution containing 59% by wt. P$_2$O$_5$ and a CaO fraction of 0.8 in the neutralizing mixture were used and also for a phosphoric acid solution with a 63% by wt. P$_2$O$_5$ content and a CaO fraction of 0.7-0.8 in the neutralizing mixture. By supplementing extraction phosphorous acid composition with microelements (Se, Cu and Zn compounds) at the stage of extraction phosphoric acid production one can obtain a product with a homogenous content of the elements, but this entails losses as high as 70-80% caused by the separation of phosphogypsum from the phosphorous material decomposition product. Because of the different mass fractions of microelement salts and feed phosphates a homogenous selenium compound content in feed phosphate is obtained only after 8 hours of mixing. Mixing time is twice shorter for copper and zinc.

**Key words:** feed phosphates, calcium phosphates, microelements

**INTRODUCTION**

Besides phosphatic fertilizers, feed phosphates are the main product of the phosphorous compounds industry. As a result of the occurrence of Creutzfeld-Jakob disease (BSE), caused mainly by the use of meat-and-bone meal for the production of feedstuffs, the industry’s interest in products based on chemical production methods (which despite the unfavourable opinions as to the impact of the manufacture process on the environment have proved to be safer in animal raising) has considerably increased. Also the modifications introduced into feed phosphate production have contributed to the attractiveness of chemical feed phosphate production technologies. The high-temperature processes or the technologies in which calcium phosphates were precipitated through crystallization (requiring filtration and the management of huge quantities of postcrystallization and washing solutions) have been replaced by processes based on the use of concentrated solutions of extraction phosphoric acid (a relatively cheap stock produced for the fertilizer industry), making it possible to simplify the technological process and reduce energy expenditures for the final drying of the phosphates and thus to improve the economic effectiveness of the industrial production of feed phosphates.$^{[1-4]}$

Considering a concept of a new feed phosphate production facility it was deemed necessary to carry out studies of the processes and unit operations involved.$^{[5-8]}$ Phosphoric acid produced for fertilizer purposes, containing at least 54% by wt. P$_2$O$_5$, was to be used for the production of feed phosphates. Because of its impurities, mainly fluorine and heavy metal compounds
(Pb, Cd, As, Hg), this product must be purified to meet the zootecnical requirements for the permissible levels of the elements\(^9\). The current all-European regulations in this field specify the permissible content of fluorine at 0.2% by wt., Cd and As at 10 mg/kg, Pb at 15 mg/kg and Hg at 0.1 mg/kg. According to the adopted concept, the phosphoric acid solution will be neutralized with a mixture of oxygen and calcium hydroxide or carbonate, whose composition will make it possible to utilize the reaction energy to maximally remove physical water from the system. Thus the thermal conditions of the process should ensure a low water content in the final product, but in view of possible polycondensation reactions of orthophosphates the process temperature should not exceed 160°C. The elimination of feed phosphate drying after the neutralization of extraction phosphoric acid with calcium compounds has an important bearing on the unit costs of feed phosphate production. Until the end of the 20th century the technological methods of manufacturing feed phosphates were as a rule based on phosphoric acid solutions with a 30% by wt. H\(_2\)O content. The water was removed in an expensive (usually nonmembrane) drying operation. This production stage was not only costly but also could increase the impurities (including dioxin) content due to the direct contact of the product with the drying gases.

Besides phosphorous and calcium, mineral feeds should also contain other indispensable micronutrient elements such as copper and zinc or ultraelements such as selenium\(^{10,11}\).

The main problem associated with feed phosphate production from higher concentrated extraction phosphoric acid solutions is the neutralization of phosphoric acid with calcium compounds (calcium oxide, hydroxide or carbonate). At a limited water content in the system the reaction proceeds in conditions characterized by increased viscosity and the presence of a solid phase. In order to achieve the proper conversion of the reagents special reactors – homogenizers or mixers (e.g. ribbon mixers) intensively agitating the reacting mixture – are used in the industry.

**REAGENTS AND INVESTIGATION METHODS**

Neutralization of concentrated extraction phosphoric acid: The neutralization process in laboratory conditions was investigated on an experimental stand based on a ceramic crucible with a capacity of 0.5 dm\(^3\) and a high-speed (1400 rpm) laboratory agitator T 25 basic ULTRA-TURRAX made by Labortechnik. Each time 100g of phosphoric acid solution with a P\(_2\)O\(_5\) content of 53.1, 58.7 and 63.0% by wt. was neutralized in the experiment. The solution was neutralized by a stoichiometric quantity of a mixture of CaO with CaCO\(_3\), in which the molar ratio of CaO to CaCO\(_3\) was respectively: 0.5:0.5, 0.6:0.4, 0.7:0.3 and 0.8:0.2. Because of the different quantities of the calcium reagents the theoretical chemical equation according to which the process proceeded had the form:

\[
H_3PO_4 + n \text{ CaO} + (1-n) \text{ CaCO}_3 \rightarrow \text{ CaHPO}_4 + \text{ H}_2\text{O} + \text{ CO}_2
\]

(1)

Value \(n\) in equation 1 corresponds to the mole fraction of CaO in the mixture of the calcium compounds.

Reagents made by POCH in Gliwice, whose purity corresponded to the ones used in analytical chemistry, were used in the experiments. In total, three series of experiments, separately for the particular P\(_2\)O\(_5\) contents in phosphoric acid, were carried out using four kinds of calcium compounds mixtures for phosphoric acid neutralization in each series. Each experiment lasted 1 hour. After cooling the reaction products were subjected to chemical analysis to determine: the total and soluble phosphorous compound contents in a 0.4% by wt. HCl solution and the physical water content. Also the maximum temperature of the reacting mixture was measured. The analytical methods applied to commercial feedstuffs were used in the investigations\(^{12}\). The physical water content was estimated, using thermal analysis (a Netzch derivatograph STA 409C), for only the water from the dehydration of calcium hydrogenphosphate hydrates. The same methodology was used to determine the CO\(_2\) content in the products on the basis of the identification decomposition reaction of the unreacted calcium carbonate proceeding in a temperature range of 860-900°C.

**Supplementation of the chemical composition of feed phosphates with selenium compounds:** The supplementation of the chemical composition of feed phosphates with selenium compounds was investigated by two methods: (1) by simulating the industrial mixing operation in a laboratory ceramic rotary mixer (30 rpm) with a capacity of 1 dm\(^3\) and (2) by using the extraction phosphoric acid production process into which a chemical compound of selenium was introduced. A 100 g sample of feed dicalcium phosphate (DCP) produced by Tessenderlo and a precisely weighed out amount of Na\(_2\)SeO\(_4\) powder, corresponding to the theoretical content of 0.05 mg Se/kg feed phosphate, were used in the mixing process. The latter was conducted for 8 hours and the selenium content was analyzed after respectively 1, 3, 5 and 8 hours. The selenium content was determined by the dianinobenzidine method exploiting the yellow colour of 3,4-diaminophenylpiazzoselenium which forms in an acid medium as a result of the reaction of soluble selenates with 3,3-diaminobenzidine\(^{13}\). The parameters of industrial extraction phosphoric acid production were simulated in laboratory conditions by conducting the decomposition of phosphoric material (Kola apatite) in a glass reactor with a capacity of 0.8 dm\(^3\), equipped
with a mechanical mixer (180 rpm), placed in a
thermostat. Phosphoric material decomposition by
sulphuric acid was conducted at a temperature of 80 ±
1°C at a liquid/solid phase mass ratio (L/S) of 2 and a
27% by wt. P₂O₅ content in the liquid phase. Apatite
and the liquid reagents (reagent sulphuric acid and
water) were fed in batches every 6 minutes, assuming
an excess amount of sulphuric acid (molarly 1.03
relative to apatite) and the theoretical course of the
process accordant with the chemical equation:

\[ \text{Ca}_5(\text{PO}_4)_3\text{F} + 5\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow 5\text{CaSO}_4\cdot2\text{H}_2\text{O} + 3\text{H}_3\text{PO}_4 + \text{HF} \]  \hspace{1cm} (2)

Decomposition was conducted for 4 hours with
0.01 g Se (sodium selenate) per 100 g of apatite added
whereby 0.16 mg Se/kg was to be obtained in the
phosphoric acid solution. A selenium level
corresponding to average animal husbandry needs
was adopted. After the phosphoric acid solution was
separated from solid phosphogypsum five liquid phase
samples were taken and the selenium content was
determined.

Investigation of the possibility of introducing copper
and zinc compounds into feed phosphates: Since feed
mineral mixtures are often supplemented with copper
and zinc compounds, investigations into the possibility
of introducing the above elements into the composition
of feed phosphates were carried out. Two options based
on similar assumptions as for selenium compounds
were tested. The first option consisted in mixing a
dicalcium feed phosphate, supplemented with copper
and zinc sulphate, in a ceramic rotary mixer. In order to
ensure a permanently stable level of the elements in the
mixture once a value close to the expected one was
achieved the test was still continued for a few hours so
that the total mixing time amounted to 17 hours. After
1, 3, 5, 10, 14 and 17 hours of mixing samples were
taken and their copper and zinc contents were
determined[14,15]. The copper content was determined by
the iodometric method – by titrating the free iodine
released in the reaction of potassium iodide with Cu²⁺
ions with sodium hyposulphite, whereas zinc was
determined complexometrically, exploiting the
formation of stable Zn²⁺ complexes with the disodium
salt of ethylenediaminetetraacetic acid. The adopted
copper and zinc contents, i.e. about 13-14 g Zn/kg P
and 3-4 g Cu/kg P, followed from the animal husbandry
recommendations.

The possibility of introducing copper and zinc
compounds at the stage of the industrial production of
extraction phosphoric acid was examined in a similar
way as for selenium compounds by simulating Kola
apatic decomposition with sulphuric acid in laboratory
conditions. The same methodology as for selenium
compounds was applied, i.e. a 3% stoichiometric excess
of sulphuric acid, a decomposition temperature of 80°C
and a liquid/solid phase ratio of 2. In accordance with
feeding recommendations, precisely weighed out
quantities of copper sulphate and zinc sulphate, whose
content after the complete transition to a liquid phase
should correspond to a level of 1.592 g Zn/kg and
0.3563 g Cu/kg in the obtained phosphoric acid
solution, were introduced into the process.

RESULTS AND DISCUSSION

Results of laboratory tests of phosphoric acid
neutralization with calcium compounds: The
chemical composition of the obtained feed phosphate
samples and the evaluated laboratory test parameters
are shown in table 1. Regardless of the experiment
conditions, a high phosphorous content in the products
in comparison with the content of this component in
commercial feed phosphates (DCP) was obtained.
Furthermore, almost all the phosphorous compounds
occurred in forms soluble in a 0.4% by wt. HCl solution
(94.5-99.8%), which are considered to be assimilable
by animals. The measured neutralization reaction
temperature exceeded 160°C already for phosphoric
acid with a 58.7% by wt. P₂O₅ content, neutralized with
a mixture of CaO and CaCO₃ with a molar fraction of
CaO as high as 0.7. High temperature levels occurred
for each of the tested experiment versions also when
phosphoric acid with a 63% by wt. P₂O₅ was used. The
physical water content in the reaction products,
relatively high for phosphoric acid containing 53.1% by
wt. P₂O₅ and a small fraction of CaO in the mixture of
calcium compounds used for its neutralization, sharply
decreased in the case of phosphoric acids with a higher
P₂O₅ content and a larger fraction of calcium oxide in
the neutralizing mixture. The CO₂ content in the
products, characterizing the reagent conversion, was
low in the experiments in which the least concentrated
(<1.4% by wt.) phosphoric acid solution was used,
whereas in the experiments in which the most
concentrated phosphoric acid solutions and the highest
CaO/CaO₃ ratios were used the CO₂ content exceeded
3% by wt. The physical water content, the process
temperature and the CO₂ content in the products
depending on the phosphoric acid used and on the
fraction of CaO in the neutralizing mixture are
illustrated in figs 1, 2 and 3.
Results of feed phosphate chemical composition supplementation with selenium compounds: The selenium content in samples taken during the mixing of feed phosphate with sodium selenate is shown in table 2. Selenium content values close to the expected ones were obtained as late as after 8 hours of mixing. After 1 hour the selenium content values differed by as much as four times between the two taken samples. The studies have shown that the mixing of two components occurring in so much different quantities is not a simple operation and takes much time. Since in feed phosphates a precisely fixed selenium content must be ensured this way of supplementing their composition with selenium is costly and not without risk.

The selenium content in the phosphorous acid solution produced during the decomposition of apatite with sulphuric acid is shown in table 3. Process specification, temperature and intensive mixing influence the obtained phosphoric acid solution’s homogeneity with regard to the selenium content. This way of supplementing the phosphoric acid composition with selenium holds promise that the selenium content will also be homogenous in the produced feed phosphate neutralized with calcium compounds. The drawback is the large loss of selenium compounds caused by the separation of phosphogypsum from the products of decomposition of the phosphorous material (apatite) with sulphuric acid. About 70% of the selenium introduced into the process involving phosphogypsum was lost. This can be avoided by dissolving sodium selenate in the phosphoric acid solution after phosphogypsum has been separated and, if need be, the selenium has been oxidized to Se(VI) with a hydrogen peroxide solution.

Results of feed phosphate chemical composition supplementation with copper and zinc compounds: Precisely weighed out quantities of loose feed dicalcium phosphate (DCP) and finely ground reagent copper and zinc sulphates were being mixed. The mixing process was only briefly interrupted at the measuring hours. The copper and zinc contents in the samples taken at the measuring hours were determined. The results are shown in table 4.

(Table 1 and 2) With UV-B radiation, biomass was increased by CaCl2 0.75%, SA and ASA 0.100% in Mianyan 26 and by CaCl2, SA, ASA 0.100% and DMSO in Huining 18, respectively.
Table 1: Results of laboratory tests of phosphoric acid neutralization with mixture of calcium compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>CaO molar fraction n</th>
<th>P2O5 Content in phosphoric acid solution % by wt. P2O5</th>
<th>Total phosphorous % by wt. P</th>
<th>P2O5 soluble in 0.4 % HCl % by wt. P</th>
<th>H2O % by wt.</th>
<th>Temperature °C</th>
<th>CO2 % by wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.5</td>
<td>53.1</td>
<td>19.98</td>
<td>19.72</td>
<td>20.27</td>
<td>141</td>
<td>0.51</td>
</tr>
<tr>
<td>2.</td>
<td>0.6</td>
<td>53.1</td>
<td>20.52</td>
<td>20.45</td>
<td>20.01</td>
<td>143</td>
<td>1.07</td>
</tr>
<tr>
<td>3.</td>
<td>0.7</td>
<td>53.1</td>
<td>20.93</td>
<td>20.29</td>
<td>15.67</td>
<td>145</td>
<td>1.22</td>
</tr>
<tr>
<td>4.</td>
<td>0.8</td>
<td>53.1</td>
<td>19.82</td>
<td>19.75</td>
<td>11.02</td>
<td>149</td>
<td>1.35</td>
</tr>
<tr>
<td>5.</td>
<td>0.5</td>
<td>58.7</td>
<td>19.97</td>
<td>19.69</td>
<td>8.40</td>
<td>154</td>
<td>0.95</td>
</tr>
<tr>
<td>6.</td>
<td>0.6</td>
<td>58.7</td>
<td>20.22</td>
<td>20.17</td>
<td>4.68</td>
<td>158</td>
<td>1.26</td>
</tr>
<tr>
<td>7.</td>
<td>0.7</td>
<td>58.7</td>
<td>20.47</td>
<td>20.37</td>
<td>4.38</td>
<td>160</td>
<td>1.99</td>
</tr>
<tr>
<td>8.</td>
<td>0.8</td>
<td>58.7</td>
<td>20.81</td>
<td>19.66</td>
<td>1.53</td>
<td>165</td>
<td>3.19</td>
</tr>
<tr>
<td>9.</td>
<td>0.5</td>
<td>63.0</td>
<td>20.50</td>
<td>20.46</td>
<td>4.65</td>
<td>161</td>
<td>0.86</td>
</tr>
<tr>
<td>10.</td>
<td>0.6</td>
<td>63.0</td>
<td>20.89</td>
<td>20.53</td>
<td>3.01</td>
<td>166</td>
<td>1.01</td>
</tr>
<tr>
<td>11.</td>
<td>0.7</td>
<td>63.0</td>
<td>20.77</td>
<td>20.71</td>
<td>2.36</td>
<td>172</td>
<td>2.89</td>
</tr>
<tr>
<td>12.</td>
<td>0.8</td>
<td>63.0</td>
<td>19.45</td>
<td>19.35</td>
<td>1.12</td>
<td>177</td>
<td>3.96</td>
</tr>
</tbody>
</table>

Table 2: Analysis of selenium content in samples taken while mixing sodium selenate with feed dicalcium phosphate

<table>
<thead>
<tr>
<th>Mixing time hours</th>
<th>Sample 1 mg Se/kg</th>
<th>Sample 2 mg Se/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.098</td>
<td>0.023</td>
</tr>
<tr>
<td>3</td>
<td>0.036</td>
<td>0.079</td>
</tr>
<tr>
<td>5</td>
<td>0.063</td>
<td>0.039</td>
</tr>
<tr>
<td>8</td>
<td>0.049</td>
<td>0.046</td>
</tr>
<tr>
<td>Expected content</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3: Selenium content in phosphoric acid solution in laboratory tests

<table>
<thead>
<tr>
<th>No.</th>
<th>Selenium content mg Se/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0475</td>
</tr>
<tr>
<td>2.</td>
<td>0.0482</td>
</tr>
<tr>
<td>3.</td>
<td>0.0478</td>
</tr>
<tr>
<td>4.</td>
<td>0.0482</td>
</tr>
<tr>
<td>5.</td>
<td>0.0479</td>
</tr>
<tr>
<td>Average content</td>
<td>0.0479</td>
</tr>
<tr>
<td>Expected value</td>
<td>0.160</td>
</tr>
</tbody>
</table>

Table 4: Analysis of copper and zinc content in samples taken during mixing of copper and zinc sulphate with feed dicalcium phosphate

<table>
<thead>
<tr>
<th>Mixing time hours</th>
<th>Zinc content mg Zn/kg</th>
<th>Copper content mg Cu/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2211</td>
<td>550.7</td>
</tr>
<tr>
<td>3</td>
<td>2710</td>
<td>731.1</td>
</tr>
<tr>
<td>5</td>
<td>2885</td>
<td>770.2</td>
</tr>
<tr>
<td>7</td>
<td>2856</td>
<td>749.4</td>
</tr>
<tr>
<td>10</td>
<td>2789</td>
<td>701.1</td>
</tr>
<tr>
<td>14</td>
<td>2828</td>
<td>769.3</td>
</tr>
<tr>
<td>17</td>
<td>2810</td>
<td>760.5</td>
</tr>
<tr>
<td>Expected value</td>
<td>2808</td>
<td>761.3</td>
</tr>
</tbody>
</table>

A copper and zinc content level close to the expected value was reached already after 3-5 hours of mixing. But at the next measuring hours deviations from the expected value were recorded. After 10 hours of mixing the copper content was lower by 7.9% and the zinc content at the 5th hour of mixing was by 2.7% higher. Considering that the requirements as to permissible deviations from the target composition are less stringent, it can be assumed that in the case of the two elements the required mixing time will be significantly shorter than for the corresponding process of enriching feed phosphates with selenium compounds.

Table 5 shows laboratory test results for introducing copper and zinc compounds in a process simulating the production of extraction phosphoric acid. After 4 hours of the decomposition of the phosphorous material with sulphuric acid the reaction products were separated into a phosphoric acid solution and solid phosphogypsum. The copper and zinc content in the liquid phase was analyzed (5 liquid phase samples were taken for analysis).

Table 5: Copper and zinc content in extraction phosphoric acid obtained in laboratory test

<table>
<thead>
<tr>
<th>No.</th>
<th>Zinc content mg Zn/kg</th>
<th>Copper content mg Cu/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>314.7</td>
<td>85.92</td>
</tr>
<tr>
<td>2.</td>
<td>318.5</td>
<td>87.32</td>
</tr>
<tr>
<td>3.</td>
<td>321.3</td>
<td>85.92</td>
</tr>
<tr>
<td>4.</td>
<td>315.4</td>
<td>89.06</td>
</tr>
<tr>
<td>5.</td>
<td>319.6</td>
<td>88.01</td>
</tr>
<tr>
<td>Average value</td>
<td>317.8</td>
<td>87.32</td>
</tr>
<tr>
<td>Expected value</td>
<td>1593</td>
<td>356.3</td>
</tr>
</tbody>
</table>

The results shown in table 5 indicate a high homogeneity of the elements content in the phosphoric acid solution. This holds promise that the feed phosphate obtained using such phosphoric acid will be characterized by a homogenous content of the elements in the product. Unfortunately, conducting the process in this way one should expect high losses in the added microelement salts as they are removed with phosphogypsum. For the laboratory test conditions the losses amounted to over 75% for the copper compounds and 80% for the zinc compounds. These products are not as expensive as selenium compounds but for
environmental reasons such a solution does not seem to be optimal.

CONCLUSIONS

Conducting the process of feed phosphates production through the neutralization of phosphoric acid solution with a mixture of CaO and CaCO$_3$, using phosphoric acid with an elevated P$_2$O$_5$ (53-63% by wt.) content and a molar fraction of CaO in the neutralizing mixture in the order of 0.5-0.8, a product with a relatively high phosphorous content (about 20% P) and a high content of phosphorous forms assimilable by animals (94-99% soluble in 0.4% HCl) was obtained. Using an elevated P$_2$O$_5$ content (at least 59%) in the phosphoric acid solution and a molar fraction of CaO in the neutralizing mixture above 0.7 a product with a physical water content of 1-4% by wt. was directly obtained whereby a drying operation in the feed phosphate production technology can be avoided.

The neutralization process temperature exceeds 160°C when a phosphoric acid solution with a P$_2$O$_5$ content higher than 59% by wt. and a CaO molar fraction of 0.8 in the neutralizing mixture are used. An elevated CO$_2$ content (> 3% by wt.) in the neutralization products is observed for phosphoric acid solution with a 59% by wt. P$_2$O$_5$ content and a CaO molar fraction of 0.8 and for phosphoric acid solution with a 63% P$_2$O$_5$ content and a CaO molar fraction of 0.7-0.8. By introducing microelement (Se, Zn, Cu) salts at the stage of production of extraction phosphoric acid one can obtain homogeneity of the microelements content in the whole volume of the product but this leads to high (70-80%) losses of the salts in the production technology. In the test conditions (a ceramic rotary mixer) the introduction of microelement (Se, Zn, Cu) salts through mixing with ready feed phosphate required about 8 hours of mixing to obtain a homogenous selenium content and a twice shorter mixing time for copper and zinc compounds.

ACKNOWLEDGMENTS

This work was supported by Polish Ministry of Science and Higher Education the National Natural Science Foundation of China (grant No 1 T09B 072 30).

REFERENCES