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Effect of the heat treatment on the morphology and sorption ability to metal ions of metallurgical slag

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The effect of the phase composition of metallurgical slag on its ability to adsorb copper ions from aqueous solutions has been investigated. Granulated slag samples, mainly amorphous, have been pre-heated at 400, 600, 800 and 1000°C, then cooled slowly in the absence of moisture. Above 600°C crystallisation of a mineral gehlenite of the melilite group and of calcium silicates of the Ca_2SiO_4 structure type begins. The appearance of crystalline phases facilitates exchange and adsorption and the amount of copper adsorbed per a gram slag increasing about 2–4 times. The important role of the crystalline phases in the slag permits the synthesis of new materials adsorbing heavy metal ions on the basis of controlled liquid slag crystallization. © *2001 Kluwer Academic Publishers*

1. Introduction

Thousands and thousands of tons of solid wastes such as slags, middling slimes and powders remain after the production of iron and steel. The greatest amount belongs to blast-furnace metallurgical slags, which makes their processing to useful products very topical.

The main method of slag processing is granulation. It consists in quick cooling of the liquid slag, due to which it cannot crystallise and forms a glassy mass. This product has hydraulic properties and is mainly used in the manufacture of cement [1]. Slag pumice and other materials are used for civil engineering purposes. The application of the slag may be widened on the basis of other properties. This material is being used as a filter or adsorbent [2, 3].

The activity of blast-furnace metallurgical slag (both granulated and ungranulated) towards various metal ions has been the subject of a series of investigations of ours [4, 5, 6]. Some regularities of the process of extracting copper, nickel, zinc, lead etc ions have been established. Ungranulated slag has shown a higher activity than the granulated one. Pre-heating of the granulated slag can enhance the adsorption capacity. We assume the phase composition to be one of the main factors determining the slag activity towards heavy metal ions.

For that reason the purpose of the present paper was to investigate the effect of the slag phase composition on its absorption capacity with respect to copper ions and, on this basis, to establish the active phase or the components determining the sorption properties of this waste material.

2. Experimental

Granulated blast-furnace slag from the firm Kremikovtsi, Bulgaria was used for the investigations. It was heated in air at 400, 600, 800 and 1000 °C in a muffle furnace. The samples were heated for 3 hours, then cooled in air in the absence of humidity, sieved and stored in a desiccrator until used. They were denoted as SL, SL-400, SL-600, SL-800 and SL-1000.

The mineral gehlenite and akermanite, which are the most typical ones in blast-furnace slag and their mixtures, were used as standards on the basis of which the results obtained after the heat treatment were compared. The reagents used for synthesizing the minerals gehlenite and akermanite were CaO, Al_2O_3 and SiO_2 or CaO, MgO and SiO_2, respectively. The oxides, taken in stoichiometric ratios (2 : 1 : 1 and 2 : 1 : 2, respectively) were ground in an agate mortar, then tabletted and heated for 6 h at 800, 1100 and 1350°C, intermediate grinding and tabletting being also performed. The mixture of gehlenite and akermanite was synthesized in a similar way, choosing an oxide ratio, which ensured formation of minerals in a 1 : 1 molar ratio.

The physicochemical characterization of the samples was carried out by the following methods:

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(i) BET method (for specific surface area determination); (ii) X-ray phase analysis with a DRON-3 X-ray spectrophotometer using K_α-Cu radiation at 0-40θ, and selectively absorbing nickel filters; (iii) XPS analysis performed with ESCALAB Mk III (VG Scientific); (iv) EPR measurements with an FRS-220 apparatus and (v) Scanning electronic microscope, type JEOL ISM - 5300 was used.

The activity of the different samples with respect to copper ions was estimated by a sorption test under static conditions. Slag (0.1 g) was mixed with 100 cm^3 solution of Cu^{2+} ions in a 16.5 mg/dm^3 concentration at initial pH 4.0. The samples were stirred for 2 hours, then the slag was removed from the solution by decanting and filtration. The Cu^{2+} concentration and the final pH (pH_f) were determined in the filtrate. The concentration of Ca^{2+} ions was also determined on some samples. The Cu^{2+} and Ca^{2+} contents in the solutions were established spectrophotometrically and complexometrically. The TM-6 pH meter was used for pH value determination.

3. Results

3.1. Characteristic of the granulated slag

The granulated slag from Kremikovtsi had the following composition (in weight %): CaO (44.0), SiO_2 (34.0), Al_2O_3 (6.4), MnO (2.4), BaO (3.5), Fe_2O_3 (0.5), and S (1.7). The density and ZPC were 2.60 g/cm^3 and 7.8, respectively, and the specific surface area, about 1 m^2/g. Some peaks were absent from the X-ray spectrum, which indicated that this material was mainly amorphous. The granulated product had a fine-cell to macro porosity.

A microscopy study of the granulated slag (Fig. 1A) has shown that not all particles have the shape of granules. Some of them were irregular porous bodies; others were coalesced to shapeless aggregates. On the basis of their colour the particles were divided into *light-grey, dark blue* and *brown*. The different structural phases of the blast-furnace slag had a characteristic colour, which was very useful for the analysis of this complex material. The X-ray spectra of the three particles type (not shown in the paper) of the granulated product chosen on the basis of their colour show that in the *light grey* one only there is a crystalline phase. The peaks in the spectra are typical of minerals of the Ca_2SiO_4 structure type [7]. The presence of the crystalline phase in these particles determines their higher activity (5.44 mg/g, Table I) towards copper ions. The results of the sorption test on the other types of particles are close and determine the sorption activity of the slag in general. Evidently, the amorphous and crystalline phases of the slag are active towards copper ions. However, this activity is stronger when the components are crystalline.

TABLE I Removal of copper ions by different particles of slag

Particles	pH_f	q_{Cu}, mg/g	Ratio Ca/Cu
light-grey	6.10	5.44	3.4
dark blue	6.15	2.83	7.8
brown	5.90	2.04	9.1

TABLE II Characteristics of the heated slag

Particle size, mm	Solid	S, m^2/g	pH	C_{Ca} mg /dm^3	q_{Cu} mg /g
<0.25	SL	1.70	6.30	11.86	13.10
<0.25	SL-400	1.30	6.15	11.01	12.60
<0.25	SL-600	1.00	7.60	16.00	16.31
<0.25	SL-800	0.85	8.20	15.50	16.17
<0.25	SL-1000	0.62	8.50	16.52	16.20
0,25–0,50	SL	0,92	5,90	12,48	2.74
0,25–0,50	SL-400°	0,90	6,10	12,16	4.00
0,25–0,50	SL-600°	0,83	6,10	12,96	7.59
0,25–0,50	SL-800°	0,26	6,10	12,14	11.35
0.25–0.50	SL-1000	0.25	6.10	12,10	11.44
0,50–1,25	SL	1,30	5,80	12,40	1.25
0,50–1,25	SL-400°	0,64	5,60	12,20	1.34
0,50–1,25	SL-600°	0,63	5,75	12,40	2.38
0,50–1,25	SL-800°	0,31	5,80	12,20	3.38
0.50–1.25	SL-1000	0.34	5.70	12.40	3.00

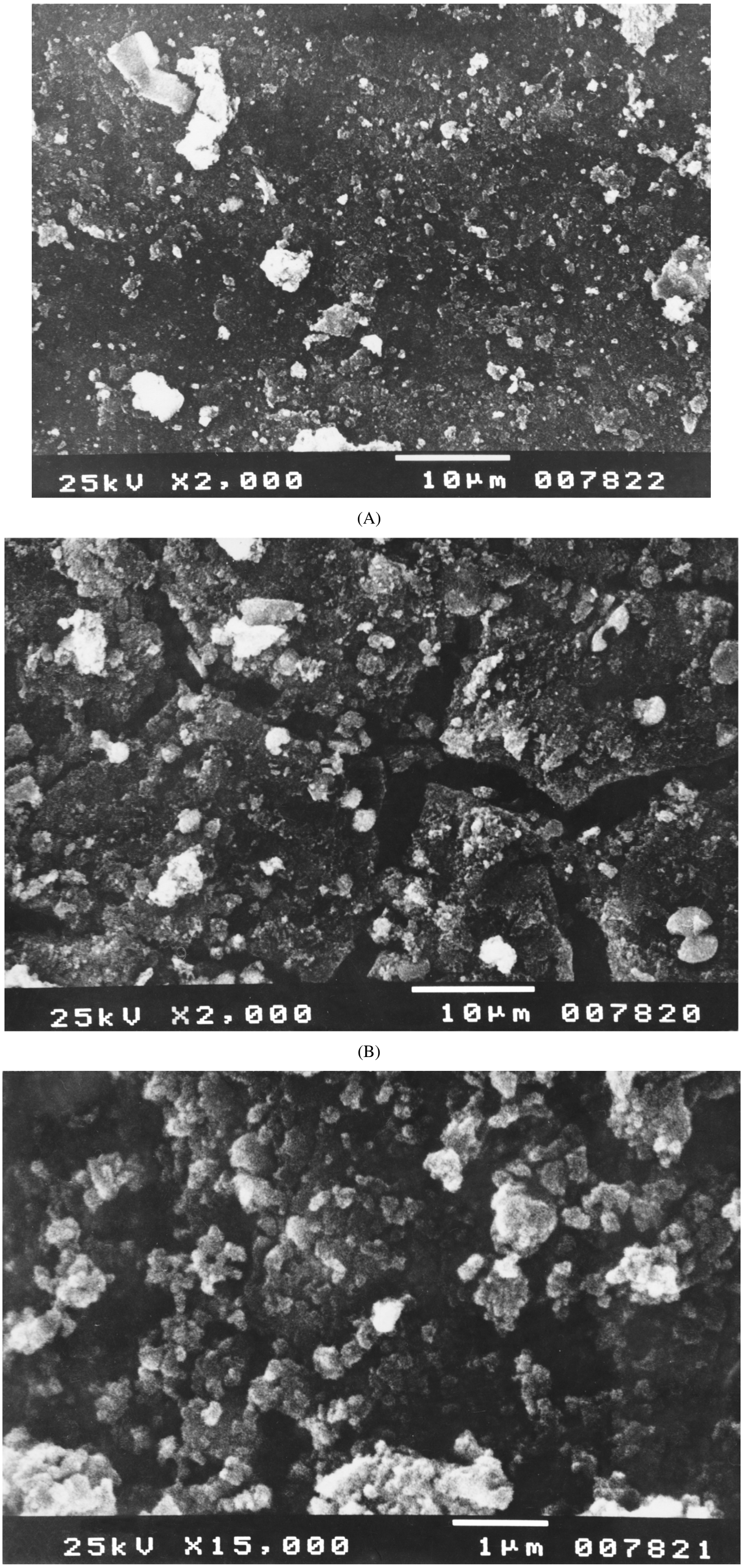
It may be expected that with the increase in amount of the crystalline phase, the slag activity would be considerably higher.

3.2. Effect of the heat treatment

Table II presents data on the surface (S), pH at the end of the process (pH_f), absorbed amount of copper ions per unit slag (q_{Cu}) and concentration of the Ca^{2+} ions passing into the solution (C_{Ca}). The data are obtained using different sizes of particles: less than 0.25 mm, 0.25–0.50 mm and 0.50–1.25 mm. The effect of copper ion removal increases with temperature of slag preheating. The largest absorbed amount of copper ions is found with the smaller-sized particles but with these particles the weakest effect of thermal treatment is observed. The adsorption of copper ions is accompanied by calcium ions passing into the liquid phase and an increase in pH by about two pH units. A more pronounced pH_f rise is observed with samples SL-800 and SL-1000 whose particle size is less than 0.25 mm. It is obvious that pre-heating affects the activity positively. However, this effect is not associated with an increase of the surface area. On the contrary, the specific surface area decreases. This is most pronounced with samples SL-800 and SL-1000 which possess the highest activity.

The scanning electron microphotograph of sample SL-800 (Fig. 1B and C) evidences serious structural changes. Larger aggregates with irregular shapes and regions with a different texture are clearly visible. This is associated with the inevitable sintering of the material at a temperature of 800–1000°C, which leads to a decrease in specific surface area of the heat-treated samples (Table II). In addition to the sintering at the above temperature, crystallization of calcium silicates, aluminum silicates and sulfides occurs.

The X-ray phase analysis has confirmed the crystallization of melilite represented mainly by gehlenite generation. The fact that the characteristic lines are very close to one another makes the identification of the minerals obtained very difficult. In addition to the distinct peaks of the above minerals there are also characteristic lines of calcium silicates and sulphides.



(A)

(B)

(C)

Figure 1 SEM photographs of granulated slag (A) with magnification of 2000× and activated slag SL - 800 at different magnifications: (B) 2000× and (C) 15000×.

TABLE III Removal of copper ions by a heat-treated slag and by the synthesized minerals

Solid	S, m^2/g	pH$_f$	C_{Ca}, mg/dm^3	q_{Cu}, mg/g
SL-800	0.47	8.20	0.33	15.30
gehlenite	0.56	9.50	–	16.30
gehlenite*		8.90	1.10	21.84
akermanite	0.43	9.40	–	16.30
akermanite*		8.70	2.80	19.04
mixture (1:1)	0.42	9.70	–	16.30
mixture(1:1)*		9.40	–	23.84

*Initial concentration of copper 24 mg/dm^3.

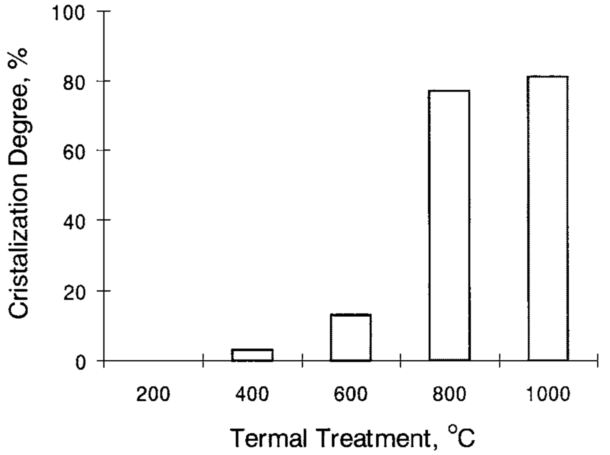


Figure 2 Relative increase of the crystalline phase depending on the temperature of pre-heating.

Fig. 2 shows the relative increase of the most characteristic line of the melilite group minerals depending on the temperature of pre-heating (d/n 2.846). Obviously, the thermal treatment favours the crystallization, i.e. the appearance of gehlenite. The maximum crystal phase content was found above 600°C.

Table III shows the results of the sorption test on sample SL-800 and on the synthesized minerals gehlenite, akermanite and their mixture. The data correspond to particles smaller than 0.25 mm. It is evident that the parameter values found for heat-treated slag and those for the synthesized minerals are close. The small specific surface area and the high pH$_f$ value should be noted.

The results of the EPR experiments are given in Fig. 3. They show the oxidation state (valence) of the copper adsorbed on the slag surface. In addition to a typical signal of Cu^{2+}, there is also a weak Fe^{3+} signal, which is obviously present in the system having a complex phase and chemical character.

In order to establish the type of the chemical compound formed on the slag surface, XPS studies were performed on the granulated sample after the adsorption process. The spectrum obtained is given in Fig. 4. Its comparison with the known spectra of various copper compounds gave no definite result.

4. Discussion

The granulated blast-furnace slag from Kremikovtsi is a complex calcium (magnesium) aluminosilicate system obtained under the conditions of abrupt cooling of the liquid phase. As was to be expected, under similar conditions the crystal phase content is negligible, i.e. below the sensitivity threshold of X-ray analysis. The sorption test showed that both the glassy and the crystalline slag particles can remove copper ions from aqueous solutions. The particles having mainly a crystalline structure are more efficient adsorbents of metal ions. However, due to their relatively low content in the granulated product, their effect is not high. This means that the slag activity towards the metal ions can be controlled. One of the ways of increasing the crystalline phase content is the control of the crystallization of the liquid slag. The experimental data indicate that crystallization sets in with the increase in the temperature of slag processing and at 800 °C a certain amount of a crystalline phase or phases facilitating sorption and exchange of metal ions are formed. The simple SL-800 adsorbs about 2–4 times more copper ions than does the untreated sample (Table II). The smallest effect of thermal treatment is observed with the smallest size of particles (below 0.25 mm). This result should be attributed to the different crystallization degrees of the particles of granulated slag. Probably the smallest particles are mainly crystalline, due to which their heating leads to no pronounced additional crystallization i.e. to no pronounced increase of the copper uptake.

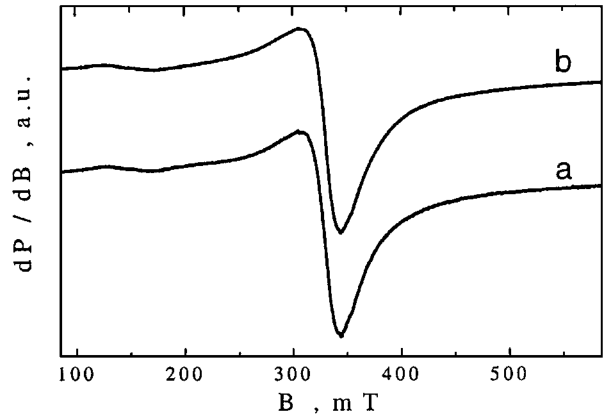


Figure 3 EPR spectra of granulated slag: a) particle size 0.25–0.50 mm; b) particle size 0.50–1.25 mm.

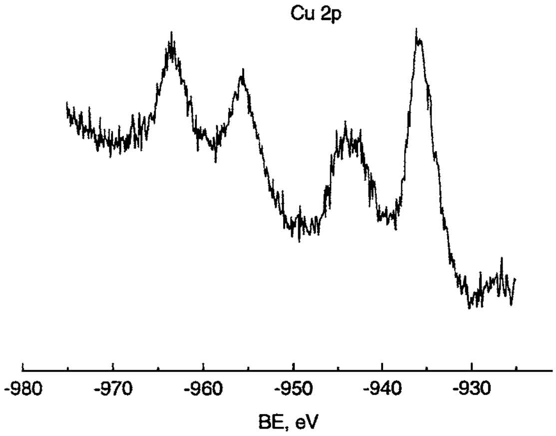


Figure 4 XPS spectra of granulated slag.

The important role of the crystalline phase in the process of copper ion elimination can be ascribed to the presence of active sites appearing during isomorphous substitution of the type Al^{3+} → Si^{4+} in gehlenite and in the aluminosilicate phases. The adsorption of metal ions (in this case, Cu^{2+}) occurs at some sites by an exchange mechanism of the type (Al, SiO^-) whose negative charge is initially compensated for by Ca^{2+} or other divalent metal ions participating in the slag composition. Under our experimental conditions (pH 4.0), participation of active surface sites of the type ($\rightarrow$SOH), where $S =$ silicon or aluminium, is also possible. Exchange between the protons of these groups and the copper ions in the solution may also occur. This is in fact a specific surface reaction, which has also been noted by other authors [8]. However, since the surface of the samples used is small, we think that the active sites of the crystal lattice play the decisive role.

The adsorption of copper ions by both the glassy and the crystalline phase is accompanied by the transition of Ca^{2+} ions from the slag to the solution. The absence of equality between the amount of adsorbed copper ions and that of the Ca^{2+} ions that have passed from the slag to the liquid phase can be explained by the competing effect of the hydrogen ions in the solution, but mainly by the inevitable hydration and hydrolysis processes of the silicates in the slag (similarly to those of the clinker minerals in cement) which are accompanied by the formation of $Ca(OH)_2$. In view of the basic character of the slag, one may assume blocking of the active sites on the surface by Ca^{2+} and/or Mg^{2+} surface ions which pass into the liquid phase on coming in contact with aqueous solutions. For that reason, the amount of Ca^{2+} ions in the solution is due not only to the $Cu^{2+} \rightarrow Ca^{2+}$ exchange but also to the above processes. The sorption process on the aluminosilicate crystalline phase can be presented schematically as follows

$$(\mathrm{Al,\ SiO})_2^- \ \mathrm{Ca} + \mathrm{Cu}^{2+} \Rightarrow (\mathrm{Al,\ SiO})_2\mathrm{Cu} + \mathrm{Ca}^{2+}$$

or

$$2\mathrm{SOH} + \mathrm{Cu}^{2+} \Rightarrow (\mathrm{SO})_2\mathrm{Cu} + 2\mathrm{H}^+$$

With the mainly glassy sample the reactivity depends, above all, on the surface, whereas with the crystalline phases sorption may take place both in the crystal lattice and the space between the crystals (intercalation). This is one of the reasons for which the activity increases irrespective of the decreasing specific surface area of the samples after heat-treatment.

The sorption of copper ions on all samples proceeded at final pH_f of about 6, i.e. higher than the pH_{in} of the solution of copper but lower than the pH value of the precipitation of the corresponding hydroxides. The heat-treated samples with the smallest particle size represent an exception. It is known that during adsorption the formation of a new phase can take place at pH values lower than those needed for its formation in the solution bulk. The results obtained by EPR and XPS studies exclude this possibility. Most probably the sorption products are metal silicates which cannot be differentiated from the solid phase.

5. Conclusion

The crystal phase in the blast-furnace slag is an important active component during the adsorption of heavy metal ions from aqueous solutions. The formation of crystalline silicates and aluminosilicates facilitates the 2–4-time increase of the sorption activity towards copper ions. The slag with a pronounced crystalline phase has adsorption characteristics close to those of the minerals of the melilite group, which are characterized by a high activity towards metal ions. The adsorption of metal ions is most favoured on samples with smaller particles. In this case the process takes place in an alkaline medium created by the material itself. On the basis of the results obtained, the exchange mechanism of metal ion adsorption is assumed to be prevailing. Depending on the conditions, a more complex mechanism including additional processes, is possible. Knowledge of the active phase permits evaluation of the adsorption properties of the slag and synthesis of new adsorbents on the basis of blast-furnace slag by means of controlled crystallization in the liquid slag.

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References

1. F. J. HOGAN and J. W. MEUSEL, *Cement, Concrete and Aggregate* **3** (1981) 40.
2. M. P. ANDRIEVSKA, O. G. CHVIDENKO, N. V. IAROCHEVSKA and L. A. KULSKI, *Chem. Technology Water* **11** (1989) 253.
3. S. K. SRIVASTAVA, V. K. GUPTA and D. MOHAN, *J. Environ. Eng.* **123** (1997) 461.
4. S. V. DIMITROVA, *Water Res.* **30** (1996) 228.
5. S. V. DIMITROVA and D. R. MEHANDJIEV, *ibid.* **32** (1988) 3289.
6. *Idem., Bulg. Chem. Industry* **69** (1998) 99.
7. ASTM, Philadelphia, 1973.
8. C. P. HUANG and E. A. RHOADS, *J. Colloid Interface Sci.* **131** (1989) 289.

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