

For organizing uninterrupted lithium and gallium supply into reactor two pressure capacities for each metal connected in parallel are provided in the device. While one capacity is functioning in another one metal is loaded and melted. While emptying the first capacity the device is switched to the second one and in the first capacity metal is prepared to the processing.

The carried out tests of the given device showed that it supports continuous obtaining of 6 l/h of liquid-metal lithium gallama with concentration of 0,8...1,0 mole/l.

Using aggregated similar developed device allows obtaining lithium gallama of specified concentration in the amount required for continuous process of alkali separation in counterflow packed column.

REFERENCES

1. Andreev B.M., Zelvenskiy Ya.D., Katalnikov S.G. Separation of stable isotopes by physicochemical methods. – Moscow: Energoatomizdat, 1982. – 208 p.
2. Tikhomirov I.A., Orlov A.A., Vidyayev D.G. Alkali separation // Zhurnal Prikladnoy Khimii. – 2003. – V. 76. – № 6. – P. 888–891.
3. Tikhomirov I.A., Lavrenyuk P.I., Orlov A.A., Vidyayev D.G. Studying the kinetics of alkali gallama decomposition in aqueous solutions of hydroxides // Zhurnal Prikladnoy Khimii. – 2002. – V. 75. – № 1. – P. 30–33.
4. Tikhomirov I.A., Orlov A.A., Vidyayev D.G. Studying gallium-lithium system viscosity // Bulletin of the Tomsk Polytechnic University. – 2003. – V. 306. – № 4. – P. 77–80.
5. Sabo K.N., Bagotskaya I.A., Grigoriev N.B. Behavior of drop gallium electrode in alkaline solutions in the area of hydrogen overvoltage // Zhurnal Fizicheskoy Khimii. – 1964. – V. 38. – № 8. – P. 2059–2061.
6. Kabanov B.N., Kiselev I.G., Astakhov I.I., Tomashova N.N. Cathodic lithium introduction into gallium in nonaqueous solution // Elektrokhemia. – 1974. – V. 10. – № 5. – P. 765–767.

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NANODISPERSED SYSTEMS IN TECHNOLOGY OF BUILDING MATERIALS AND UNITS

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The examples of obtaining nanodispersed systems and materials have been given. It is shown that nanodispersed systems are formed at hydration of binders, clay minerals, immediate silica dissolution in soda, different carbonates dissolution in carbonic acid etc. Control of nanodispersed system formation process and using materials obtained artificially in these processes is the main task of structural material science.

Building material technology is connected inseparably with use of disperse systems consisting of solid, liquid and gaseous phases (S + L + G). The main task of the technology is conversion of free-dispersed systems that is the systems with mobile solid phase into connected-dispersed state as a result of serial transformation of the original coagulation structure into condensed one and then into the structure of higher order and strength – crystallization one.

The distinctive feature of building material technology on the basis of dispersed systems is constant presence of solid phase in the system regardless of liquid and gaseous phase presence. Solid phase is a carrier of the main property of building materials – strength; it takes part in

Conclusions

The stages of phase reversal at alkali segregation by chemical exchange method in the systems LiGa-NaOH and LiGa-KOH have been studied.

Pilot laboratory devices for intermittent and continuous obtaining lithium gallama in metal melts were developed and tested. It was shown that the latter of the stated devices provides obtaining lithium gallama of the specified concentration of 0,8...1,0 mole/l in the amount required for implementation of continuous column process of alkali segregation.

The possibility of organizing phase reversal in gallama-exchange systems LiGa-NaOH and LiGa-KOH and manifold multiplication of single separation effect of alkalis in packed columns was showed.

5. Sabo K.N., Bagotskaya I.A., Grigoriev N.B. Behavior of drop gallium electrode in alkaline solutions in the area of hydrogen overvoltage // Zhurnal Fizicheskoy Khimii. – 1964. – V. 38. – № 8. – P. 2059–2061.
6. Kabanov B.N., Kiselev I.G., Astakhov I.I., Tomashova N.N. Cathodic lithium introduction into gallium in nonaqueous solution // Elektrokhemia. – 1974. – V. 10. – № 5. – P. 765–767.

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formation of all three types of the above mentioned structures. Solid phase particles are elementary «bricks» which are required for different structures formation; the strength of the latter are predetermined first of all by dispersion and grain-size composition of the particle. The less the particle the less internal defects they contain and such particle presence in the original disperse systems is obligatory. In structure of prepared original dispersed systems (cement paste and solutions, gypsum paste, molding compounds and mixtures, different suspensions etc.) two constituent parts should be distinguished: structural frame formed by coarsely dispersed particles and pore substance consisting of fine dispersed particles and liquid phase placed in pore space of coarsely disper-

sed frame. Colloid-chemical properties of pore substance, its content in the system influence greatly on strength formation of different structures.

In colloid chemistry, the disperse systems and surface phenomena science [1] the systems with mobile solid phase are divided into three groups:

1. Ultra-micro-heterogeneous with particle size of 1...100 nm.
2. Micro-heterogeneous with particle size of 0,1...10 mkm.
3. Coarsely dispersed with particle size of 10 mkm.

Systems of the first group may be called nano-dispersed with good reason and they form together with particles of the second group (up to 500 nm) with liquid phase the pore substance or suspension in various building mixtures.

Materials with particles of nanodispersed size are mainly obtained by the following artificial methods [2]:

1. Solid phase dispersion at milling in jet-type and jar mills and spraying in atomizers or at fast-rotating disks of sols or salt solutions.
2. Plasma-chemical technique at evaporation and condensation of various substances.
3. Electroarc method accompanied also by evaporation and condensation of substances.
4. Evaporation and condensation with chemical reactions at volatile chloride (SiCl_4) hydrolysis and oxidation, thermal decomposition of hydrocarbons and metal oxidation in gaseous media at oxide smoke formation.
5. Precipitation or coprecipitation of sols, salt solutions by hydroxide solutions.
6. Salt thermal decomposition.
7. Electric explosion of metals and conductors [3].

In natural conditions the existence of substances in nanodispersed state is rather problematical due to their thermodynamic instability. Nevertheless, rocks of sedimentary origin (clays, chalk, diatomite) contain substances capable of forming nanodispersed systems with water at condensation structures conversion into coagulation ones. First of all such conversion is typical for some clays and clay materials (collyrite, montmorillonite, hydromicas etc.) having large value in technology of building materials on the basis of clays.

A significant disadvantage of artificial techniques of obtaining nanodispersed materials is their rather low capacity and therefore nanopowders wide application in building technologies is rather problematical. The exception is the technologies in which nanodispersed materials are formed as a by-product and the example of this is microsilica forming at obtaining ferrosilicon in EAF. From 50 to 250 kg of microsilica with real density of 2200 kg/m^3 and specific surface up to $40 \text{ m}^2/\text{g}$ is formed per 1 ton of ferrosilicon [4]. Total volume of the formed microsilica amounts to 25 thousand tons/year only at «Kuznetskie ferrosplavy». Average-surface size of microsilica particles amounts to 68 nm and total part of particles with the size of 200 nm amounts to 50 %, particles up to 500 nm – 96 %.

The unique property of microsilica is high value of total free surface energy (U_F) which is made up of Gibbs energy (surface unit) and latent heat of forming new surface unit [1]:

$$U_F = \sigma + q_F = G_F + T S_F,$$

where σ is the specific free surface energy, $\sigma = dG/dF$; G_F is Gibbs energy of surface unit; q_F is the latent heat of forming new surface unit, $q_F = T S_F$; S_F is the excess entropy of surface unit; T is the temperature.

The peculiarities of microsilica particle construction and excess of free surface energy stipulate its high chemical activity. For example, reaction of sodium silicate formation from solution of sodium hydroxide and microsilica occurs intensively at standard conditions with high heat release. The similar reaction with native, crystal silica may occur only at pressures 1...1,5 MPa and temperatures 180...200 °C. While forming soluble sodium silicate (liquid glass) both amorphous and crystal silica are additionally dispersed to the state of high-concentrated lyosol being also nanodispersed system occurs.

Liquid glass is rather perspective raw material for obtaining foam-silicate noncombustible heat-insulating materials with rigid structure and density of $80...300 \text{ kg/m}^3$, strength of 0,15...0,85 MPa and heat conductivity coefficient of 0,04...0,08 $\text{W/m}\cdot\text{°C}$ [5, 6]. Foam, granulated material – silipore with heat conductivity coefficient of 0,028...0,035 $\text{W/m}\cdot\text{°C}$ and density of $10...60 \text{ kg/m}^3$ is also obtained on the basis of liquid glass [7]. Obtaining highly porous materials on the basis of liquid glass is stipulated by considerably high dispersion of sodium-silicate groups in its composition that allows forming interpore partitions with the thickness to 5...10 mkm in foam material.

Water solutions of liquid glass may be also used for obtaining highly dispersed powders by sedimentation method of calcium chloride with solution or other salts. At sodium silicate interaction with calcium chloride the exchange reaction occurs at formation of hydrosilicates of calcium and silica gel. The ratio of the reaction products is predetermined by stoichiometric ratio of the original reacting agents and dispersion – by original solution concentration. If the exchange sedimentation reaction is carried out with soluble salts Cu, Ni, Fe, Co, Cr, Mn then volume-painted powders of various colors may be obtained [8].

Powders obtained in this way may be used as an additive into dry building mixtures, porous and dense concretes as crests as well as polymer and silicate paints.

Recently microsilica is wider used at obtaining high-strength (90...140 MPa) concretes. High reactivity of microsilica allows combining calcium hydroxide (portlandite) forming at hydration of mineral-silicates at general temperatures of cement hardening. As a result more stable and less soluble in water calcium hydrosilicates are formed that influences profitably on such construction properties of concrete as water and frost resistance and durability.

The same effect is achieved at introduction of small quantities of liquid glass (0,25...0,5% from cement mass) into concrete. Portlandite formed at initial period of hydration interacts with sodium silicate forming hydro-

silicates of calcium and silica gel which later combines intensively portlandite at general hardening temperatures. Overdose of liquid glass into concrete is undesirable as it results in forming excess silica gel which forms friable, incapable of hardening coagulation structures.

Use of liquid glass at manufacturing slag-alkaline and porous concretes is rather perspective [9]. Slag-alkaline binding ones possess a complex of unique construction properties overbalancing cement properties that allows making high-strength and durable concretes. High features of concrete are stipulated first of all by the formed hydration products in which zeolite like minerals practically insoluble in water are predominant.

In contrast to nondispersed systems (solid+gas) obtained by physical methods the technique of obtaining nanodispersed systems with liquid (S+L) is more productive and less power-consuming as solid phase at this technique is formed due to the chemical sedimentation reactions and physicochemical processes of solution and hydration. The example of this is the processes of obtaining silica gel at liquid glass neutralization with acids, salts and alkalis, calcium hydrociliates and other metals at interaction of salt solutions, bases with liquid glass solution. At reactions of immediate water addition by oxides of calcium and magnesium the fine-dispersed calcium and magnesium hydroxides respectively are formed. The hydration reaction of hemihydrate plaster at the ratio S:L=1:10 during which the original hemihydrate plaster which forms stable colloid system is dispersed is of certain interest. Using it at aerocrete production allows stabilizing the process of its porization and increasing construction characteristics of finished products [10]. Excess of free surface energy of gypsum microparticles evenly distributed in the original aerocrete mixture is consumed for formation and crystallization of ettringite, which needle crystals reinforce inter-pore partitions in aerocrete and increase its strength.

Nanodispersed powder of calcium carbonate [11] which may be used for improving rheological properties of finishing compounds on the bases of dry building mixtures and plasters are obtained by calcium carbonate dissolution in carbonic acid and further thermal decay (>100 °C) of formed calcium dicarbonate.

The process of forming nanodispersed system in the initial period of cement hydration when particles of permolecular level of dispersion are formed (1...5 nm) [12] containing not less than three unit cells and possessing phase properties is of utmost importance. Particles of such dispersion level at different chemical composition possess common feature – a very extended surface which amounts to 350...450 m²/g [13]. At real density of hydration primary products 1,5...2,2 g/cm³ the average-surface particle size amounts to 6...11 nm.

Formation of primary hydrated particles of nanodispersed size and their further combining due to the reciprocal coalescence in the conditions of appearing restricted state is more common feature of cementing property demonstration for all binding systems. Since the moment of combining primary particles firstly the coagulation and then crystallization structures of cement

stone start forming. This process is accompanied by considerable time decrease of hydration products specific surface.

Formation of primary nanodispersed system at cement hydration is also confirmed by the character of thermokinetic curves [14, 15]. Primary, the most intensive peak of heat release is stipulated by decrease of free surface energy of solid phase and heat of wetting release. The processes of hydrolysis of C₃S and other materials hydration contribute also into this heat release. Duration of this heat release amounts about 0,5...1 h, that is comparable with duration of cement setting initial time. The beginning of cement setting is stipulated by appearance of nanodispersed hydrated particles which bind considerable part of mixing water and due to increase of volume concentration of solid phase in the system cement-water its plastic strength starts increasing. During the setting time the adsorption binding of all free water occurs and the system cement-water obtains solid state and considerable strength. Motive force of brick materials interaction with water is predetermined by the value of total thermal effect of two constituents: hydration thermal effect Q_H and thermal effect of destruction and dispersion of mineral crystal lattice Q_C

$$\Delta Q = Q_T + (-Q_K).$$

Hydration heat is positive as the formation of bond between two atoms or ions is always accompanied by enthalpy decrease (exothermic process). Process of destruction and dispersion of crystal lattice accompanying by bond opening in crystal is always connected with heat absorption (endothermic process) and value Q_C is negative. If $Q_H > Q_C$ then $\Delta Q > 0$ and heat excess is consumed for temperature increase of cement-water system that is observed at cement wetting with water. At crystal dispersion heat spent for crystal lattice destruction overbalance hydration heat $\Delta Q < 0$ and system temperature decreases. This phenomenon is observed in induction period of cement hydration when in isolated conditions the temperature of cement-water system is 3...4 °C lower than dry cement temperature.

Formation of primary nanodispersed products is of great importance for stable temporal progress of cement hydration process as disorder degree in the system increases at dispersion and the course of hydration process is supported by entropic factor. At the same time if the course of cement hydration process was stipulated only by entropic factor then considerable decrease of system temperature would be observed. Really such phenomenon is not observed and after a certain decrease of system temperature in induction period (entropic factor dominance) in 4...6 h after cement contact the system temperature start increasing owing to heat release at binding primary nanodispersed particles into larger and more stable aggregates as well as heat released at interaction of dipoles and water ions with unhydrated particle surface (enthalpy factor predominance).

The ratio of enthalpy and entropic factor values in cement-water system supports negative value of Gibbs energy for a long time of hydration process and different in signs thermal effects of combination process for na-

nodispersed particles (+) and surface dispersion of cement grains (–) stimulate a stable course of brick mineral interaction with water including induction and further periods of cement hydration.

It should be mentioned that cement particles are mainly dispersed owing to protonation of near-surface and surface layers of particles. Hydrogen ions (protons) formed at electrolytic dissolution of water molecules at prime contact with cement particles possess anomalously high mobility ($3,26 \cdot 10^{-5}$ m/s) and high penetrability as their sizes are enormously (Table) less than the sizes of crystal lattice of brick minerals. Protons penetrating into mineral crystal lattice are bound by resistant hydrogen bond with electronegative oxygen atoms and form hydroxylion. Besides, protons undergo ion exchange reactions with mineral cations ($\text{Ca}^{2+} \leftrightarrow 2\text{H}^+$ etc.) with the result that primary molecules of $\text{Ca}(\text{OH})_2$ the size of which is comparable with sizes of main mineral crystal lattice together with hydroxylion are formed; and owing to this the wedging destruction of cement particle surface layer occurs forming nanodispersed hydrated particles.

Table. Comparative sizes of crystal lattice of minerals and ions

Mineral	Unit cell sizes, ion, nm	Mineral, ion	Unit cell sizes (ion), nm
C_2S	0,5...0,7	CaO	0,48
C_3S	1,4...2,5	Ca (OH) ₂	0,36...0,49
C_3A	1,5	OH ⁻	0,306
C_4AF	0,53...1,45	H (atom)	0,106 (atom)
H_2O	0,27	H ⁺	$1,2 \cdot 10^{-6}$

Constant dispersion of cement original particles, formation and agglomeration of nanodispersed hydrated particles in setting time results in filling up the free porous surface of cement-water system, appearing the excess inner pressure and restricted state which stimulate the development of recrystallization process of primary hydration products into more stable state with density of 2,4...2,6 g/cm³. By the end of setting time at thermokinetic curve the recrystallization process is characterized by considerable heat release and in this time cement grout is fastened and rather strong crystal frame of cement stone is intensively formed. Content of capillary-stationary water (maximal molecular moisture) in cement grout defined by high-absorbency media technique [16] (compression of cement grout cake with water-to-cement ratio 0,3, thickness of 1...2 mm, placed between two packs of filter paper, at pressure of

6,55 MPa during 10min) amounts to 12...13 % during the whole setting period and only by the end of setting time increases sharply up to 17 %. This fact is also confirmed by recrystallization process and indicates that water in primary hydrated products is retained by adsorption forces up to the end of setting time and only at recrystallization the stable crystalline hydrated compounds are formed.

Increase of hydration product density at their recrystallization results again in appearing of free porous surface in the system and free water which interacts with nonhydrated cement particles and such hydration cycle is repeated with decaying intensity for a long time.

Hydration processes and processes of cement hardening are deeply interrelated and they may be controlled only on the basis of detailed analysis of these processes mechanism. If the motive force of hydration process is the difference of thermal effects of processes of water attaching by solid phase and dispersion of primary cement particles then motive force of hardening process is the increase of solid phase volume content in the system owing to formation of hydrated products. Therefore, to accelerate hardening process it is necessary to intensify the formation process of primary nanodispersed system due to the change of water ionic composition, control of its adsorption properties, by application of electrophysical methods of external influence and amplification of dispersion process by additional heat introduction to the system. The strength of cement stone and articles on its base may be increased by organizing uniform crystal structure at the moment of recrystallization of primary hydration products owing to introduction of cement crystallizers (crents) being in nanodispersed state (microsilica, liquid glass, bi-water nanodispersed plaster, preliminary obtained calcium hydrosilicates and hydroaluminates etc.).

On the basis of the above-stated the conclusion may be made that practically all techniques of obtaining building products (foam and dense concretes, clay and silicate brick, different items on the basis of semiaquatic plaster, foam-and gas-silicates, foam-silicates on the basis of liquid glass etc.) are accompanied by formation of nanodispersed systems being of great importance while forming optimal structures with specified properties. Joint use of such systems and nanodispersed materials obtained artificially in technology of building materials and articles is rather actual task of modern building material science.

REFERENCES

1. Frolov Yu.G. Course of colloid chemistry. Surface phenomena and disperse systems. – Moscow: Khimiya, 1989. – 464 p.
2. Morokhov I.D., Trusov L.I., Chizhik S.P. Ultra-disperse metal media. – Moscow: Atomizdat, 1977. – 264 p.
3. Nazarenko O.B. Electric-explosive nanopowders: obtaining, property, application. – Tomsk: TSU Press, 2005. – 148 p.
4. Snitko Yu.P., Plyukhin S.B., Pavlov S.F., Stepanov V.I., Serdyukov S.P. Utilization of dry dust from ferrosilicium production // In the collected articles: Improvement of ferrosilicium production. Materials of industrial scientific and technical conference. – 3rd issue. – Novokuznetsk, 1997. – P. 349.
5. Pat. 2173674 RF. IPC C04B 28/26, 111/20. Composition and way of obtaining swollen silicate material / V.A. Lotov, V.I. Vereshagin, Yu.A. Stalmakov. Stated 13.08.1998; Published 20.09.2001. Bull. № 26. – 4 p.
6. Pat. 2268248 RF. IPC C04B 28/26, 111/40. Foam material and technique of its production / V.A. Lotov, K.A. Rudik. Stated 06.07.2004; Published 20.01.2006. Bull. № 02. – 5 p.
7. Gorlov Yu.P. Technology of heat-insulating and acoustic materials and articles. – Moscow: Vysshaya Shkola, 1989. – P. 177–180.
8. Pat. 2133218 RF. IPC C01B 33/12. The technique of obtaining finely dispersed powders / V.A. Lotov, Yu.V. Pasechnikov. Stated 17.02.1998; Published 20.07.1999, Bull. № 20. – 5 p.

9. Glukhovskiy V.D., Pakhomov V.A. Slag-alkali cements and concretes. – Kiev: Budivelnik, 1978. – 184 p.
10. Pat. 2173674 RF. IPC C04B 38/02. Composition of mixture for manufacturing nonautoclave aerocrete / V.A. Lotov, N.A. Mitina. Stated 09.11.2004; Published 10.05.2006, Bull. № 02. – 5 p.
11. Pat. 2268242RRF. IPC C01F 11/18. The way of obtaining superdispersed calcium carbonate / A.P. Smirnov, V.A. Lotov. Stated 05.01.2004; Published 20.01.2006, Bull. № 02. – 4 p.
12. Ratinov V.B., Rosenberg T.I. Additives into concrete. – Moscow: Stroyizdat, 1989. – P. 29–36.
13. Butt Yu. M., Sychev M.M., Timashev V.V. Chemical technology of binding materials. – Moscow: Vysshaya Shkola, 1980. – P. 340–344.
14. Grankovskiy I.G. Structure formation in mineral binding systems. – Kiev: Naukova Dumka, 1984. – P. 105–110.
15. Mchedlov-Petrosyan O.P. Chemistry of inorganic building materials. – Moscow: Stroyizdat, 1988. – 304 p.

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ADSORPTION OF AZITHROMYCIN DIHYDRATE AT STATIONARY MERCURY AND SOLID ELECTRODE

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Adsorptive component in oxidation and renewal processes at different types of electrodes for antibiotic-macrolide azithromycin dihydrate has been studied. Adsorption parameters for azithromycin oxidation processes at glass-carbon electrode and for renewal processes at mercury-film electrode were calculated.

Introduction

Voltamperometric behavior of antibiotic of macrolide series of azithromycin dihydrate (azithromycin) should be studied for developing new more ultimate techniques of quantitative chemical analysis. The importance of developing such techniques is stipulated by the fact that the given antibiotic refers to the second generation of semisynthetic antibiotic of macrolide series. Presence of nitrogen atom in its structural formula defines azithromycin into a separate class of azalides. Antibiotic possesses high microbiological and clinical efficiency in treating a number of serious infections of breathing passages, skin and soft tissues, some urogenital infections. In connection of their high therapeutic efficiency preparations having azithromycin dihydrate as a reactant are the most adulterated ones on the market of pharmaceuticals.

It is shown in the paper [1] that azithromycin oxidation process at glass-carbon (GC) electrode and renewal process at mercury-film (MF) electrode seem to be complex processes with more than one electron complicated not only by additional intermediates but probably adsorption processes.

Earlier other authors have not carried out investigations on studying azithromycin adsorption. However, the results of such investigation are required for improving metrological performances of the technique of quantitative chemical analysis. It should be mentioned that there are not many methods for studying adsorption process of organic compounds and for its quantitative assessment. All these methods have considerable restrictions in electrode selection; many of them are implemented exclusively at «liquid» (MF) electrodes.

Experimental part

Experimental technique

To choose operating conditions of determining azithromycin the modern voltamperometric analyzer STA was used.

Quartz cup with base electrolyte 0,02 M Na₂HPO₄ with volume of 10,0 ml was placed into electrochemical cell of voltamperometric analyzer and indicator glass-carbon electrode, chloride silver reference electrode and one more glass-carbon electrode as an indicator one set into proper connectors of electrochemical cell were put into solution.

With the help of the programs STA and VAM [2] the survey regime of voltamperogram was selected and anode voltamperogram of background was recorded. Aliquot of process solution of azithromycin dihydrate was added and voltamperogram was recorded again at the same conditions.

The character of dependence of current magnitude of azithromycin electro-oxidation at GC electrode on electrode cure time in solution indicates the presence of adsorption processes (Fig. 1). If electrode after curing during some time (15...30 min) in azithromycin solution without overlapping polarizing voltage was transferred into electrolyzer with background solution and sediment electro-oxidation was carried out then the peak of this sediment electro-oxidation was observed; the current magnitude in this case was equal about 1/3 of current magnitude recorded before at the electrode in solution containing azithromycin that is confirmed by literary data [3].