Chemistry for Sustainable Development **12** (2004) 565–571

Potential Utilizations of Soda Production Wastes

A. A. SHATOV, M. A. DRYAMINA and R. N. BADERTDINOV

Soda Company, Ul. Babushkina 7, Sterlitamak 453122 (Russia)

E-mail: ntc@sodastr.bashnet.ru

(Received May 16, 2003; in revised form June 30, 2004)

Abstract

Methods for utilization of liquid and solid wastes of soda production are reviewed. The possibility of flooding oil fields with distiller fluid is examined. A landfilling technique is described whereby distiller fluid is injected into deep horizons. Utilizations of distiller fluid in asbestos-cement and white black productions are discussed. From soda production sludge one can manufacture building materials and oil-well cement materials for cementing wells under stringent mining and geological conditions.

INTRODUCTION

Using the ammonia technique in soda ash production leads to an economical process, yielding a high quality product. Along with soda, however, this process gives a large quantity of production wastes – so-called distiller fluid in the form of highly mineralized suspension, which is a serious disadvantage of the method. Sludge (solid waste) is separated, while clarified (liquid) wastewater is continuously discharged into river and is thus a source of water basin pollution with chloride ions. Therefore, utilization of soda production waste and creation of a wasteless process for soda ash production remain to be challenges in this field, although this method has long been in use.

Waste utilization is an acute problem not only for the Soda Company, but also for large-tonnage soda productions in general. Of various means of utilization of distiller fluid, methods for the preparation of $CaCl_2$ and NH_4Cl are most popular [1–5]. However, these are not solutions to the problem because the demand for the first product (oil and chemical industry, municipal engineering) is relatively low, and the consumption of the second product (agriculture) is limited by the low content of nitrogen (24–25 %).

Currently, there are various methods for utilization of soda production wastes. For example, using distiller fluid in the production of asbestos-cement articles substantially accelerates consolidation of asbestos-cement at the initial stage of the process; this method also makes it possible to lower the medium temperature in the conveyor from 70 to 60 °C, to decrease vapor consumption, and to improve the geometrical parameters of the sheets.

Distiller fluid also serves as raw material for the preparation of white black. This process enables utilization of 22–25 m^3 of distiller fluid per 1 t of white black. The Soda Company employs this method for the production of one of the brands of white black.

Using distiller fluid for lime milk production by lime slaking is another direction of utilization of the former. The process yields lime milk with improved qualities such as higher fluidity, higher rate of lime slaking, *etc.* provided that the water to distiller fluid ratio is kept equal to 3 : 1.

For landfilling, distiller fluid is pumped through enlarged injection wells constructed by using bore holes or special procedures for treatment of subterranean horizons (subterranean nuclear explosion). Landfilling is done to the Lower and Middle Carboniferous carbonate strata 500 m thick lying at depths of 1760–2260 m.

For soda production, a wasteless procedure has been developed for processing distiller fluid to yield a $CaCl_2$ composite consisting of $CaCl_2$ and NaCl [6, 7]. The composition is useful for drilling, maintenance, and repairing works during oil and gas production. Moreover, the salt composition is employed for road icing control in municipal engineering.

Analysis of methods for purification and utilization of wastewaters at soda enterprises shows that sludge utilization is the least explored point [6, 11]. This problem was treated by scientists and specialists from different countries. Thus in 1938 the Solvey Concern (Germany) started research at a soda plant in Bernburg; the aim of these studies was to remove $CaCl_2$ and NaCl from distiller fluid precipitates, to reduce moisture in the precipitates for utilization of the latter, and to manufacture portland cement, silicate articles, binding materials, cellular concrete, and road coatings from the precipitates. Works had been pursued until 1974, but the results have not found industrial application [12].

Researchers from the "Carbonate" Scientific and Industrial Company (Kharkov) offered a procedure for sludge processing to obtain a meliorant for liming of acid and solonetz soils or to prepare mineral feed additives to mixed fodder for various species of poultry [13]. Work in this direction is now continued by Polish researchers.

It was suggested [14] that the solid residues of wastewaters at soda producing enterprises be utilized as the raw material component of alinite clinker. This possibility, however, has not been realized either.

Researchers from Ufa suggested sludge processing for the preparation of cementless binding materials [15]. This gave an impetus to further work, which resulted in the construction of a sludge processing pilot plant (Soda Company).

Preparation of binding materials for use in various fields of industry (in particular, in oil-well cement production) is one of the promising trends in sludge utilization. As is known, cement stone hardening under hydrothermal conditions is often accompanied by changes in the characteristics of stone, resulting from thermal destruction caused by phase transitions of highly basic, thermodynamically unstable hydrate compounds into more stable low basic substances [16, 17]. The oil refining application of belite-siliceous oil-well cement materials prepared from soda production sludge by co-roasting with a silica-containing component (sand) was validated, both theoretically and experimentally, based on previous data [18], available knowledge on the hardening of basic clinker components [19], and estimates of thermodynamic stability of calcium hydrosilicates at elevated hardening temperatures (>100 °C) [20].

The goal of the present work is to study prospects for utilization of soda production sludge with a view to use it in building materials production.

EXPERIMENTAL

Soda production wastewaters are forwarded to sludge tanks where sediments are allowed to settle and accumulate [7]. Sludge contains 40–60 % moisture. Tables 1 and 2 list the chemical and mineralogical compositions of sludge.

Regarding particle-size distribution, sludge is powder where 60.5 % of all particles are less than 0.05 mm and 4.2 % are more than 1.0 mm in size.

Processes that occur in the system have been investigated. The composition of the mixture was chosen based on calculated data (73–80 % solid residue, 14–24 % sand, which corresponds to the ratio $CaO : SiO_2 = 2 : 1$).

RESULTS AND DISCUSSION

High-temperature X-ray and thermography studies revealed that below c. 600–630 °C the composition of the batch mixture remained unchanged. At 1000 °C the peaks of $CaCO_3$ vanished, while the peaks characteristic of the γ-modification of $2CaO \cdot SiO_2$ (γ-C_2S) appeared. The amount of γ-C_2S increased with

TABLE 1

Chemical composition of sludge, %

Component	Content	Component	Content
CaO_{tot}	42.88	Cl^-	5.03
Including:		R_2O_3	2.37
CaO_{act}	6.81	SO_4^{2-}	9.04
CaO_{inact}	0.3	Na^+	1.07
MgO_{tot}	8.68	Hydration moisture	6.65
CO_2	22.18		
SiO_2	2.1		

Note. Sludge density 1.152 g/cm^3, S : L = 1 : 42.

the roasting temperature. After cooling, the compound transformed into the β-modification of dicalcium silicate (β-C_2S). The roasting product had a finely granular structure, the β-C_2S crystals being irregular round grains sized 1–2.5 μm. The γ-modification of dicalcium silicate was not found, and self-dispersion caused by the polymorphic transformation of β-C_2S into γ-C_2S was not observed. The β-C_2S form was probably stabilized due to its finely crystalline structure. The reaction rate between CaO and SiO_2 was low; when the roasting temperature was raised to 1100 °C, the β-C_2S content increased from 13 to 25 %. The mixture contained unchanged CaO and SiO_2.

Decarbonization and mineralization promoting additives are used to accelerate clinker formation processes. The mechanism of additive action is as follows. At lower temperatures, a layer of melted mineralizer or eutectic melt of mineralizer and components of the batch mixture is formed at the boundary of particle contact in the latter. The most effective additives are chlorine-containing reagents, in particular, $CaCl_2$. The latter is highly reactive in a melt because the activation energy of the clinker-forming oxides decreases by a factor of 10 and the diffusion coefficient increases by several orders of magnitude. In addition, the temperature of the polymorphic transformation of quartz into reactive tridymite decreases considerably.

The introduction of $CaCl_2$ in the batch mixture is explained by the presence of this compound in the "fresh" (not yet treated with wash waters in drainage tanks) residue. The X-ray diffraction patterns recorded at 680 °C contained the lines of $CaCO_3$, while the peaks of $CaCl_2$ vanished because calcium orthochlorosilicate $CaSiO_4Cl$ formed. At 940 °C the diffraction maxima of $CaCO_3$ disappeared, and spurrite $Ca_3(SiO_4)_2$ manifested itself on the diffractogram; CaO peaks appeared and became stronger at 1000 °C due to decomposition of spurrite; also, the peaks of dicalcium silicate appeared, while the lines corresponding to SiO_2 decreased to a minimum. The diffractograms recorded at 1100 °C contained the peaks of only two minerals: dicalcium silicate and CaO. The reflections of calcium orthochlorosilicate and spurrite were absent. β-C_2S was obtained as irregular crystals 3–5 mm in size, and its content increased to 60–65 %. The roasting product also had a finely granular structure. The bending strength of the one-day samples autoclaved at 170 °C varied from 6 to 10 MPa depending on the roasting temperature and time and on the content of $CaCl_2$. The interaction was accelerated or retarded depending on the combination of the roasting temperature and $CaCl_2$ content. This called for optimization of the composition of the binder and roasting mode.

The optimal composition of the binder was found to be as follows: 73–80 % solid residue of soda production wastes, 14–24 % siliceous additive, and 3–6 % $CaCl_2$. The optimum roasting temperature is 1000–1100 °C. After roasting, the product is subjected to grinding [21].

Since the binder contains active CaO, for solutions based on belite-siliceous oil-well cement materials the dehydration factor is up to 2 %. For comparison, for a solution based on ShPTsS-120 and employed under the same conditions, this factor is 7.8 % (at 22 °C) and 4.5 % (at 150 °C); for a solution based on ShPTsS-

TABLE 2

Mineralogical composition of sludge, %

Mineral	Content	Mineral	Content
$CaCO_3$	50.4	NaCl	2.7
$CaSO_4$	12.8	SiO_2	2.1
$Ca(OH)_2$	8.9	R_2O_3	2.4
$Mg(OH)_2$	12.5	Hydration moisture	3.0
$CaCl_2$	5.2		

200, 10.1 and 8.3 %, respectively. In 30 min after the belite-siliceous oil-well cement solution had been tempered, the amount of free water (determined by evaluating the limiting water loss for a differential pressure of 5 MPa at 150 °C) was 20–26 % lower than that in slag solutions. The latter hardened with shrinking deformations, while the former increased by up to 1.6 % in volume. Adhesion between the cement stone and rock samples increased by a factor of two or three. Heat resistance was evaluated from variation of the strength characteristics of the stone and phase composition of the hardening products with time. After seven days of hardening at 120, 150, and 180 °C, the bending strength increased from 3.6 to 4.2 MPa (compression strength increased from 8.9 to 14.3 MPa). Thereafter the strength characteristics remained constant in the range 10.4–14.2 MPa depending on the water content and hardening temperature. The phase composition of the seven-days hardening products mostly includes hydrosilicates of tobermorite $4CaO \cdot 5SiO_2 \cdot 5H_2O$, xonotlite $6CaO \cdot 6SiO_2 \cdot H_2O$, and $CaO \cdot SiO_2 \cdot H_2O$ (CSH(B)) types, which accounts for heat resistance of the stone.

Based on these results, a technological scheme for the production of belite-siliceous oil-well cement (Specs TU 406.412-84) has been developed, and pilot batches have been manufactured and successfully employed for cementing hydrothermal ("Sakhalingeologiya" Company) and oil ("Gurievneftegazgeologiya" and "Aktyubneftegazgeologiya") wells.

Applicability of belite-siliceous binders to the production of silicate articles has been analyzed. For compacted silicate articles, a binder with a hydraulic modulus of 2.73 and increased CaO_{free} content seems to be optimal. Samples with 10 % binder have high strength, both as crude (0.56 MPa) and autoclaved (35 MPa) specimens. The presence of $CaCl_2$ in the silicate mixture had a pronounced effect on the building properties of the samples. When its content increased to 1.0 %, the softening factor decreased from 1.07 to 0.81 for 0.2 % $CaCl_2$ and from 0.93 to 0.77 for 0.4 % $CaCl_2$. The phase composition of the hardening products includes tobermorite and xonotlite – the minerals that impart high mechanical stability and lasting quality to articles. Compacted silicate samples based on the belite-siliceous binder are characterized by strength that increased from 35 to 45 MPa within a certain period of time (generally one month) after autoclave treatment. For samples with 0.4 % $CaCl_2$, strength increased from 32 to 35 MPa, and for those with 1.0 % $CaCl_2$, it decreased to 22 MPa. In the latter case, no salting-out has been observed on the surface of $CaCl_2$ samples [22, 23].

Industrial tests showed that bricks had the following characteristics: medium brand M 125; frost resistance 25; binder consumption 420-460 kg per thousand conventional brick units. Brick completely satisfied GOST 279–79 "Brick and silicate stones" Specs. The given technology for the production of silicate brick using the belite-siliceous binder based on soda production wastes was introduced at the Sterlitamak plant of building materials, which manufactured over 65 million conventional brick units.

Pilot batches of oil-well cement were produced at the pilot plant for sludge processing of the Soda Company for cementing wells under stringent mining and geological conditions [24-27]. Trials were accomplished according to GOST 1581–85 Specs and led to the following results:

1. Low-temperature, sedimentation-resistant, and nonshrinking oil-well cement based on sludge and clinker (no gypsum). The composition of the oil-well material and a solution on its basis: up to 90 % portland cement clinker, up to 10 % baked sludge, 0.1–0.13 % plasticizing additive, and up to 5 % calcined soda.

The material satisfies the following requirements [28] to the chemical composition of the binder, %: 17.74 SiO_2, 3.43 Al_2O_3, 4.04 Fe_2O_3, 67.29 CaO, including 22.12 CaO_{act}, 2.01 MgO, 0.11 Cl^-, 1.76 SO_3, and 3.62 hydration moisture.

The physicochemical properties of the oil-well solution (stone) are: specific surface 3500 m^2/kg; stiffening time – start 11.40 a. m., end 7.00 p. m.; ultimate bending strength is 1.4 MPa for a two-day sample at a hardening temperature of 5 °C, 2.7 MPa for a 28-day sample, and 2.5–2.9 MPa for a two-day sample at (20 ± 2) °C; water loss factor 2.0 %.

2. The oil-well cement is sedimentation-resistant, nonshrinking, and light-weight, and is based on a clinker waste with a finely disperse

silica-containing additive (10 % of the mass of the dry mixture). The chemical composition of the binder, %: 21.93 SiO_2, 9.93 Al_2O_3, 3.84 Fe_2O_3, 59.32 CaO_{tot}, including 24.53 CaO_{act}, 3.37 MgO, 0.17 Cl^-, and 1.44 SO_3.

The physicomechanical properties of the oil-well solution (stone): specific surface 3500 m^2/kg; stiffening time – start 3.00 a. m., end 4.20 a. m. at (75 ± 3) °C and start 10.00 a.m. end 6.00 p.m. at (20 ± 2) °C for W/C (water to cement) = 0.9; ultimate bending strength is 2.64 MPa for a two-day sample at (75 ± 3) °C and 2.17 MPa at (20 ± 2) °C. The water loss factor is 0.3 %. The composition of the oil-well material: 75–80 % portland cement clinker, 5–10 % production waste, 10 % finely disperse silica-containing mineral additive.

Introduction of a mineral filler in the binder yields oil-well solutions with a density of 1500–1650 kg/m^2. For the filler we used white black (Soda Co.) with a specific surface of 110 m^2/g.

Successful trials of oil-well cement materials were performed at industrial companies "Arktikmorneftegazrazvedka" and "Eniseyskneftegazgeologiya".

Appropriate treatment of sludge forms a lime-containing binder, which is useful as a building material for the production of cellular concrete [29]. The production process involves thermal treatment (900–1000 °C) of the solid waste of soda production, drying natural quartz sand, and subsequent co-grinding of these components to a specific surface of 4000–5000 cm^2/g; then semihydrate gypsum $CaSO_4 \cdot 0.5H_2O$ was added to retard hydration of the binder and promote grinding, and water was added for partial hydration of CaO. Frost resistance of the resulting cellular concrete units is at least 35 frost resistance units, and compression strength is at least 3.5 MPa. The units are designed for outer and inner blockwork and for laying partition walls in residential, public, agricultural, and auxiliary industrial buildings and installations with relative humidity maintained at 75 %.

Gas concrete units are hardened by treatment with saturated steam in an autoclave. This is accompanied by complex physicochemical processes, occurring as a result of chemical interaction between CaO and SiO_2, forming calcium hydrosilicates varying in basicity and crystallinity. Under conditions of autoclave treatment in one of widespread modes, the $CaO–SiO_2–H_2O$ system undergoes transformations: formation of highly basic calcium hydrosilicates $2CaO \cdot SiO_2 \cdot H_2O$ [$C_2SH(A)$], changing into low-basic CSH(B), tobermorite, xonotlite, and gyralite ($C_4S_6H_5$). The stated hydrosilicates, possessing useful properties, are responsible for the strength and long-life of the hydrosilicate materials. Thus compression strength can reach 12 MPa, which depends on bulk weight (from 300 to 800 kg/m^3). Raw material consumption rates, t/m^3 of articles: 0.756 for binder, 0.00068 for aluminum powder, and 0.017 for gypsum binder.

Around 30,000 m^3 of small wall blocks have been manufactured during the period of plant operation. In 1985 experimental residential buildings with outer walls 30 cm thick were constructed by the "Ishimbaizhilstroy" trust (design from the "Bashgrazhdanstroy" Instutute) in Urman-Bishkadak and Skvorchikha villages; the buildings are still functioning and were found to be in a satisfactory state. Moreover, dozens of animal husbandry and auxiliary buildings were erected in many regions of Bashkiria.

Numerous attempts aimed at utilization of sludge from soda industry as a filling material for asphalt-concrete mixtures failed because of the high contents of water-soluble NaCl and $CaCl_2$ in sludge [30, 31]. Hydrophobization of solid residues did not provide a solution to the problem of sludge utilization in asphalt concretes [30]. Removal of water-soluble compounds from solid residues is rather labor-consuming.

A rational solution to the problem is addition to the solid residue of mineral components in quantities reducing the contents of water-soluble compounds to admissible limits in the filler. These include quartz sand, limestone, ash from heat stations, and other mineral fillers containing no water-soluble compounds and alkalis. Since the mixture of the solid residue and the mineral component should be subjected to grinding it is desirable that the mineral component should be fragile and finely divided.

A number of filler powder brands (for example, Ps-OP, Ps-OK, Ps-03) with at least

50 % solid residue and 25–50 % mineral component have been developed under laboratory and industrial conditions. Each brand should satisfy the following requirements: up to 6 % water-soluble salts, up to 2 % alkaline oxides, up to 5 % $CaCl_2$, bitumen capacity no more than 100 g/100 cm^3, humidity up to 1 %, grain size up to 1.25 mm.

Trials of asphalt concretes prepared from limestone (granulometry "G" according to GOST 9128–76) with a solid residue powder (A type) or its mixtures with mineral components (B type) gave the following results [32]: rather high strength at different temperatures was exhibited by asphalt concretes with A type fillers; water saturation and swelling are within standard values, water resistance factor of asphalt concrete with B type fillers (quartz sand, limestone, ash from heat stations) exceed the standard values.

The cracking temperature of asphalt concretes with B type fillers and mineral components is 8–13 °C lower than that of asphalt concrete with a limestone mineral powder or cement dust. This is because the solid residue contains hydration water, freezing at very low temperatures. Thus using the B type powder filler affords asphalt concretes with the major characteristics satisfying the standard values and with improved crack resistance compared to that of asphalt concretes with conventional fillers. Due to this, the working life of asphalt concretes with the suggested powder is, on the average, four years longer than that of asphalt concretes with a limestone mineral powder or cement dust. Trials were conducted at "Bashkiravtodor" industrial company and "Bashzavodneftestroy" trust (Ufa).

Thus we have described the utilizations of soda production sludge after preliminary thermal treatment. Of great interest, however, is using crude (unroasted) sediments. For this purpose, utilization of unroasted solid residues in cement-based masonry and plastering mortars has been examined [33]. Introduction into building mortar of an optimal quantity of waste as an inorganic plasticizing additive instead of lime paste improves the plasticity of the mixture and ensures the required strength and frost resistance. Wastes should better be introduced into building mortars of M 25, M 50, M 75, and M 100 brands (according to strength). The average density of mortars with wastes should be over 1500 kg/m^3, adhesion of mortar with the support at least 1.5 kg/cm^2, and waste content in the raw mix of building mortars up to 240 kg/m^3 of the mortar. Thus for M 50, consumption of materials is (kg/m^3): cement 195, wastewaters ($\rho = 1480$ kg/m^3) 134, sand 1530, and water 221. The cement : wastewater: sand ratio (by volume) is 1:0.51:5.78. The flow of the mortar is 9 cm. Industrial trials of these building mortars in the Soda Company and "Sterlitamakstroy" trust showed encouraging results.

To expand the applicability of soda production sludge (including slimes after brine purification and minor lime slaking waste) studies were carried out to examine other applications. In particular, other potential applications include building cements, dead-burned magnesia, fillers for polymer materials, putties, and chemically precipitated chalk.

A positive decision has been taken concerning patent grant for the method for the preparation of chemically precipitated chalk from soda production wastes and intermediates [34, 35].

CONCLUSIONS

Possibilities for utilization of soda production sludge have been examined based on experimental studies.

A process for the production of belite-siliceous oil-well material with a dehydration coefficient of 2 % has been developed; the material enlarges upon hardening by 1.6 % (in volume) and has two or three times better adhesion of cement stone to rock samples than that inherent in slag slurry.

Availability of solid wastes obtained in large quantities at soda enterprises in several regions of this country makes it possible to set up production of silicate articles using belite-siliceous binder and production of building materials from cellular concrete without using traditional raw materials such as cement, lime, and other binding agents.

Utilization of sludge as a filler for asphalt-concrete mixtures with additions of the mineral component has been discussed.

It was found that unroasted solid wastes may be added to the building slurry as inorganic plasticizing additives instead of lime paste. If introduced in amounts corresponding to a cement : wastewaters : sand volume ratio of 1 : 0.51 : 5.78, the waste ensures the required strength and frost resistance.

Thus the above-discussed technologies provide not only chemical products in demand with customers, but also solutions to environmental problems encountered by enterprises that produce soda ash by the ammonia method.

REFERENCES

1 I. N. Shokin, S. A. Krasheninnikov, Tekhnologiya sody, Khimiya, Moscow, 1975, 287 p.
2 S. A. Krasheninnikov, Tekhnologiya kaltsinirovannoy sody i ochishchennogo bikarbonata natriya, Vysshaya shkola, Moscow, 1985, 287 p.
3 V. I. Maksin, O. Z. Standritchuk, L. M. Petrenya, *Zh. prikl. khim.*, 51, 11 (1988) 2424.
4 I. P. Narkevich, V. V. Pechkovskiy, Utilizatsiya i likvidatsiya otkhodov v tekhnologii neorganicheskikh veshchestv, Khimiya, Moscow, 1984, 239 p.
5 A. A. Furman, Neorganicheskiye khloridy, Khimiya, Moscow, 1980, 416 p.
6 A. A. Shatov, Utilizatsiya tverdykh i zhidkikh otkhodov proizvodstva sody na osnove sterlitamakskogo PO «Soda,» Abstr. of papers from the Int. Symp. at the Int. Exhibition «Chemistry-92,» Moscow, 1992.
7 A. A. Shatov, *Khimiya i tekhnologiya vody*, 14, 5 (1992) 367.
8 A. A. Shatov, Ispol'zovaniye tverdykh otkhodov sodovoy promyshlennosti v proizvodstve vyazhushchikh, stenovykh i drugikh stroitel'nykh materialov, Abstr. of papers from the 7th Int. Symp. on Soda Industry, Torun, Poland, 1988.
9 G. I. Mikulin, I. K. Polyakov, Distillyatsiya v proizvodstve sody, Goskhimizdat, Leningrad, 1956, 348 p.
10 N. P. Tabunshchikov, Proizvodstvo izvesti, Khimiya, Moscow, 1974, 239 p.
11 S. A. Krasheninnikov, Tekhnologiya sody, Khimiya, Moscow, 1988, 304 p.
12 Ispol´zovanie otkhodov sodovoy promyshlennosti, Rev. inform. of the Bernburg Soda Plant, Bernburg, 1976, 12 p.
13 Puti povysheniya stepeni ispol´zovaniya syr'ya v sodovoy promyshlennosti, Rev. inform., series «Soda Industry», NIITEKhIM, Moscow, 1986, 35 p.
14 B. I. Nudelman, Tverdye ostatki sodovogo proizvodstva – syr´evoy komponent alinitovogo klinkera, Tashkent, 1986, VINITI deposit No. 3707-86, Moscow.
15 Ya. S. Amirov, R. N. Gimaev, Kh. B. Rakhmankulov, Ispol´zovanie vtorichnykh resursov v strtoitel´stve i okhrana okruzhayushchey sredy, Bashk. kn. izd-vo, Ufa, 1986, 192 p.
16 E. I. Ved, G. M. Baklanov, E. F. Zharkov, Fiziko-khimicheskiye osnovy tekhnologii avtoklavnykh stroitel´nykh materialov, Budivelnik, Kiev, 1966, 88 p.
17 V. S. Danyushevskiy, R. M. Aliev, I. F. Tolstykh, Spravochnoye rukovodstvo po tamponazhnym materialam, Nedra, Moscow, 1987, 373 p.
18 V. M. Kravtsov, Tamponazhnye materially dlya krepleniya skvazhin v slozhnykh geologo-tekhnicheskikh usloviyakh, Author´s Abstract, Technical Sciences Doctoral Dissertation, Ufa, 1984, 47 p.
19 A. F. Polak, V. V. Babkov, E. P. Andreeva, Tverdeniye mineral´nykh vyazhushchikh veshchestv, Bashk. kn. izd-vo, Ufa, 1990, 216 p.
20 O. P. Mchedlov-Petrosyan, Khimiya neorganicheskikh stroitel´nykh materialov, Stroyizdat, Moscow, 1988, 265 p.
21 Pat. 1689321 USSR, 1991.
22 Pat. 1076410 USSR, 1984.
23 Pat. 1622318 USSR, 1991.
24 Pat. 1555465 USSR, 1990.
25 Pat. 2059791 RF, 1994.
26 Pat. 2059792 RF, 1994.
27 Pat. 2059793 RF, 1994.
28 Pat. 2072027 RF, 1994.
29 Yu. I. Merkulov, A. A. Oratovskaya, A. A. Shatov, V. V. Babkov, Izdeliya iz gazobetona dlya sel'skogo stroitel´stva. Otkhody proizvodstva v stroitel'stve, Bashk. kn. izd-vo, Ufa, 1983, 104 p.
30 G. K. Syuni, Dorozhny asfal´tovy beton, Nauk. Dumka, Kiev, 1986.
31 I. A. Rybiev, Asfaltovye betony, Vysshaya shkola, Moscow, 1969, 264 p.
32 Pat. 1381099 USSR, 1988.
33 Rekomendatsii po primeneniyu neobozhzhennogo tverdogo ostatka otkhodov sodovogo proizvodstva v stroitel'nykh rastvorakh, USSR Union of Sci. and Eng. Soc., Bashkir Department, Ufa, 1990, 19 p.
34 RF Application No. 2002120165, 24.07.02.
35 RF Application No. 2002120166, 24.07.02.