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TREATMENT OF USED QUENCHING SALTS

A new installation allowing treatment of the used quenching salts is presented. This treatment is based on precipitation of barium sulphate in the solution of used quenching salts due to solid ammonium sulphate addition. The method designed makes it possible to process these wastes into two useful products: barium sulphate and a solution that can be usable for the production of liquid mineral fertilizers. The by-product of this method, solid waste, is practically non-toxic and can be used during the production of building materials. In the pilot installation designed, 10 Mg of used quenching salt that contained 60 mass % of $BaCl_2$ was processed. Working parameters of the installation were characterized and the properties of the products obtained (barium sulphate, fertilizer solution and solid waste) were discussed. The influence of temperature, residence time, the concentrations of barium, calcium, sodium and potassium chlorides in the feeding solution on barium sulphate growth rate and crystal size was determined.

NOTATION

B – nucleation rate, $s^{-1} \cdot m^{-3}$,
B_{rc} – nucleation rate (reaction – crystallization), $s^{-1} \cdot m^{-3}$,
b – nucleation rate order,
c_{eq} – saturation of solution, $mol \cdot dm^{-3}$ or mass %,
CV – coefficient of variation defined as (standard deviation/mean size)·100%, %,
$\Delta c = c - c_{eq}$ – supersaturation, $mol \cdot dm^{-3}$,
D – crystallizer diameter, m,
d – draft tube diameter, m,
g – growth rate order,
G – crystal growth rate, $m \cdot s^{-1}$,
G_{rc} – crystal growth rate (reaction – crystallization), $m \cdot s^{-1}$,
H – crystallizer height, m,
h – draft tube height, m,
h_p – vertical distance from a propeller agitator to a bottom, m,
k_b – nucleation rate constant,
k_g – growth rate constant,

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L – characteristic crystal length, m,
L_m – mean size of crystals, m,
L_{50} – median particle size (50% cumulative weight undersize), m,
M_T – suspension density (total mass of particles per unit volume), kg · m^{-3},
n – population density (number of crystals per unit size per unit volume of the system), m^{-1} · m^{-3},
q_v – volumetric flow rate, m^3 · s^{-1},
T – temperature, K,
V_t – total capacity of crystallizer, m^3,
V_w – working capacity of crystallizer, m^3,
[...]   – concentration of salt in feeding solution, mass %,
ε – porosity,
z – concentration of solid particles in suspension, mass %,
τ – mean residence time defined as V_w/q_v, s.

1. INTRODUCTION

During metal quenching treatment various mixtures of chemical compounds are often in use, usually: barium, calcium, sodium and potassium chlorides [1]. The chemical composition of quenching salts varies depending on their type and purpose. The contents of barium chloride, sodium chloride and calcium chloride vary from a few to almost 100 mass %, from 10 to over 50 mass %, from a dozen or more to about 50 mass %, respectively, and that of potassium chloride reaches up to a dozen mass % [2]. The used quenching salts after cooling form a hard mass difficult to dissolve which is considered as one of the most troublesome industrial wastes [3], [4].

Storage of such used quenching salts is associated with the hazard for environment because of uncontrolled migration of heavy metals to the soil and surface waters (that may occur through trickling or rinsing out from badly safeguarded or damaged storage places). The used-quenching waste comprises barium chloride, which is easily soluble in water and whose lethal dose approaches 10 mg/kg of bodyweight [5], therefore it is simply imperative to develop a method of utilization of this toxic waste. An effective solution to this problem not only brings the benefits resulting from environmental protection but also allows the recovery of valuable components contained in the waste. Processing of such wastes is in accordance with the Waste Act [6], which states that the wastes' manufacturers are obliged to reuse wastes when it is technologically and economically reasonable.

The idea of used quenching salts utilization was developed on the basis of laboratory experiments. The chemical compositions of average samples of these salts taken in plants, where heat metal working took place, were defined (table 1). The physicochemical properties of relevant wastes, their solubility in water along with the composition of the solution and insoluble residue were determined. The conditions of barium sulphate precipitation by means of solid ammonium sulphate addition were studied, particular process parameters were determined and

the possibility of separating a suspension was tested (crystal size distribution, filtration rate).

Table 1

The element composition of average used quenching salt samples
taken from some metal heat treatment plants

Composition	Waste from plant						
	A	B	C	D	E	F	G
Element	Content in mass %						
Ba	40.50	53.14	28.47	21.80	35.60	33.20	27.80
Fe	9.79	4.76	39.87	0.01	1.87	3.57	0.29
Ca	3.98	1.13	16.06	0.23	3.98	1.10	2.96
Na	3.85	4.07	0.14	4.41	1.68	0.79	6.03
Mg	0.15	0.01	0.44	0.05	0.18	1.19	< 0.01
K	0.75	4.34	–	6.34	0.18	0.14	0.11
Al	0.41	0.02	3.93	0.07	0.05	0.09	< 0.01
B	0.16	< 0.01	0.11	–	0.03	0.03	< 0.01
Mn	0.02	0.02	0.08	0.09	0.01	0.01	< 0.01
Mo	0.18	0.09	0.03	–	–	–	–
Cu	0.03	< 0.01	0.05	0.01	0.01	0.01	0.01
Zn	0.03	< 0.01	0.06	< 0.01	–	–	–
Cd	–	–	< 0.01	–	–	–	0.77
Cr	0.11	0.06	0.04	0.03	0.02	0.02	< 0.01
Ni	0.03	0.02	0.21	0.02	0.02	0.01	< 0.01
Pb	0.005	0.003	0.011	–	–	–	–
Sr	0.10	0.10	0.11	0.12	0.05	0.05	0.05
Ti	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	–

The technological concept developed was checked on a model scale (simulation of the actual production process), and then the experimental production system [7] was designed and constructed. 10 Mg of used quenching salt of the composition "A" (table 1) were processed in that system. On this basis the system for used quenching salts industrial processing was designed.

The results of the investigation of used quenching salts processing on laboratory, model and pilot scale are presented below. This technology is based on the barium sulphate precipitation by means of crystalline ammonium sulphate(VI) from the solution obtained after waste quenching salts dissolved in water. This is a typical crystallization process with simultaneous chemical reaction of precipitation of sparingly soluble barium sulphate (solubility product: $1.1 \cdot 10^{-10}$) [8]. Running the process in a controlled way that maintains proper conditions of reaction, nucleation and crystals growth [8]–[11] allows us to obtain the product of the quality required and its further usage [12].

2. BARIUM SULPHATE PRECIPITATION AND CRYSTALLIZATION

Continuous crystallizer with internal circulation of suspension of working capacity of 0.6 dm^3 was used for the barium sulphate precipitation. It was a cylindrical glass tank (V_t = 1 dm^3, D = 120 mm, H = 123 mm) with a draft tube (d = 57 mm, h = 53 mm) placed in its axis. Inside this tube three-paddle propeller agitator (h_p = 7 mm) was mounted. During all experiments the number of agitator revolutions was constant (7 s^{-1}), hence the circulation inside crystallizer could be considered as stable and intensive enough. Figure 1 shows IKA/LR-A1000 test stand diagram controlled by a computer [13].
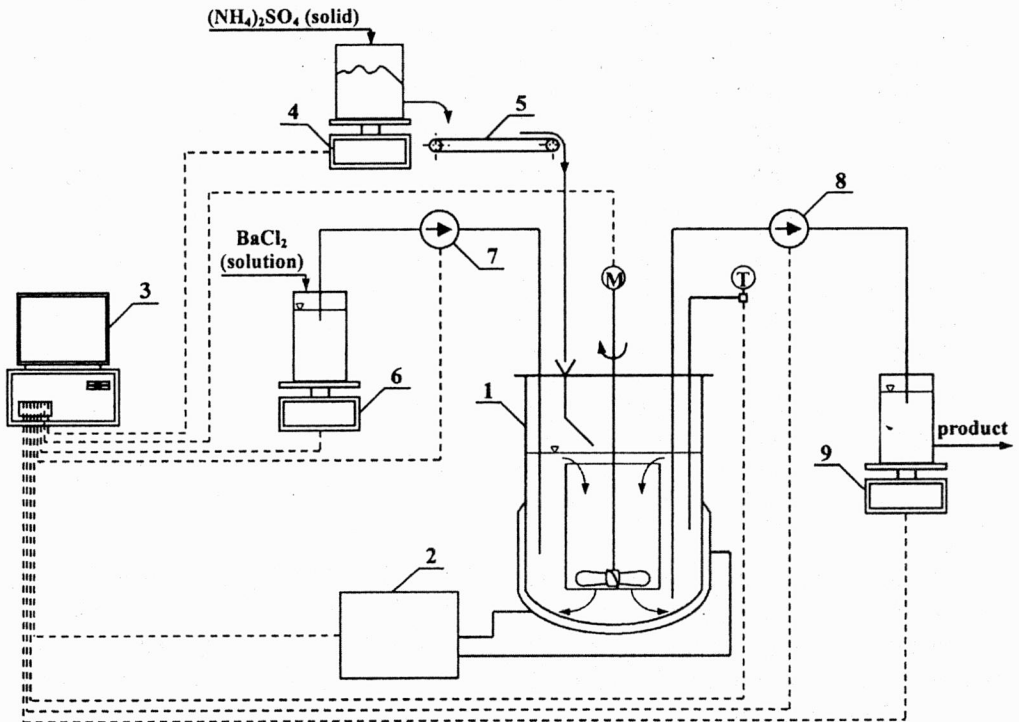

Fig. 1. Experimental setup of the continuous crystallizer:
1 – crystallizer, 2 – thermostat, 3 – computer, 4, 6, 9 – balance, 5 – feeder,
7, 8 – pump, M – stirrer speed control, T – temperature control

The crystallizer was fed with barium chloride solution (pump 7) and solid ammonium sulphate (weighed amount balance 4 and feeder 5) under stoichiometric conditions. The feed points were as follows [14]: solution – between reactor vessel and draft tube; solid $(NH_4)_2SO_4$ – the surface of circulating suspension close to agitator (figure 1). After the crystallization parameters had been stabilized the process was

conducted for 7τ. After this period, the solid phase content (M_T, z, ε) in the product suspension, mother liquid chemical composition and barium sulphate crystal size distribution (CSD) were determined.

The growth rate of barium sulphate crystals and their size depend on precipitation and crystallization temperature, barium ion concentration in the feeding solution (crystal contents in the suspension) and the residence time of a suspension in the crystallizer (supersaturation) [15]:

$$G_{rc} = 2.05 \cdot 10^{-13} T^{2.84} M_T^{-0.34} \tau^{-0.86}, \tag{1}$$

$$L_m = 3.19 \cdot 10^{-13} T^{3.05} M_T^{-0.36} \tau^{0.11} \tag{2}$$

for: $313 < T < 348$ K, $115.4 < M_T < 292.8$ kg $BaSO_4/m^3$ ($10.0 < [BaCl_2] < 24.0$ mass %), $900 < \tau < 3600$ s. Figure 2 shows the influence of a temperature on crystal size in the $BaSO_4$–NH_4Cl–H_2O system. This figure proves that within the investigated range of parameters mean size of barium sulphate crystals was lower than 10 µm.
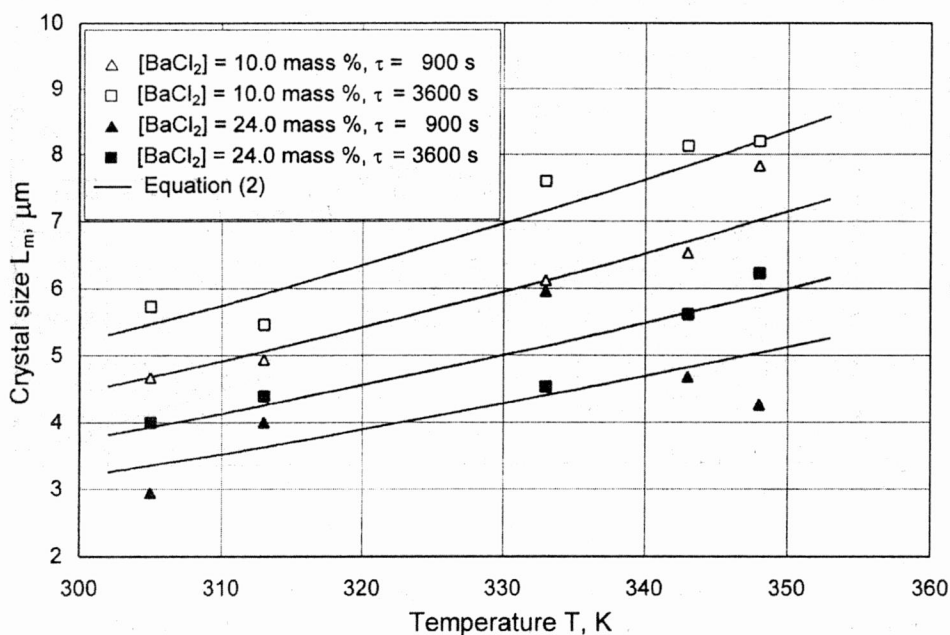

Fig. 2. The influence of temperature on the mean size of barium sulphate crystals

The rates of nucleation and crystal growth were estimated based on the crystal size distribution (CSD). For that purpose the calculation procedure for ideal MSMPR crystallizer (Mixed Suspension Mixed Product Removal) was applied [16]. This is

a reasonable approach [17]: relation between the density of crystals population and their size can be approximated for by linear plot in $\log(n)$–L system for $L > 2$ μm. For the crystals of a size $L < 2$ μm the departure from those assumptions was noticed. There may be many reasons for this phenomenon: growth rate dispersion, size-dependent growth, the dependence of a crystal size factor on crystal size, or simply incorrect mixing in the crystallizer with a circulating suspension. In the simplest assumed model of nucleation and crystal growth kinetics, these processes were neglected. Growth rate can be calculated with an error not higher than 15%. Figure 3 shows an example of the size distribution of barium sulphate crystals for the precipitation and crystallization parameters being recommended.
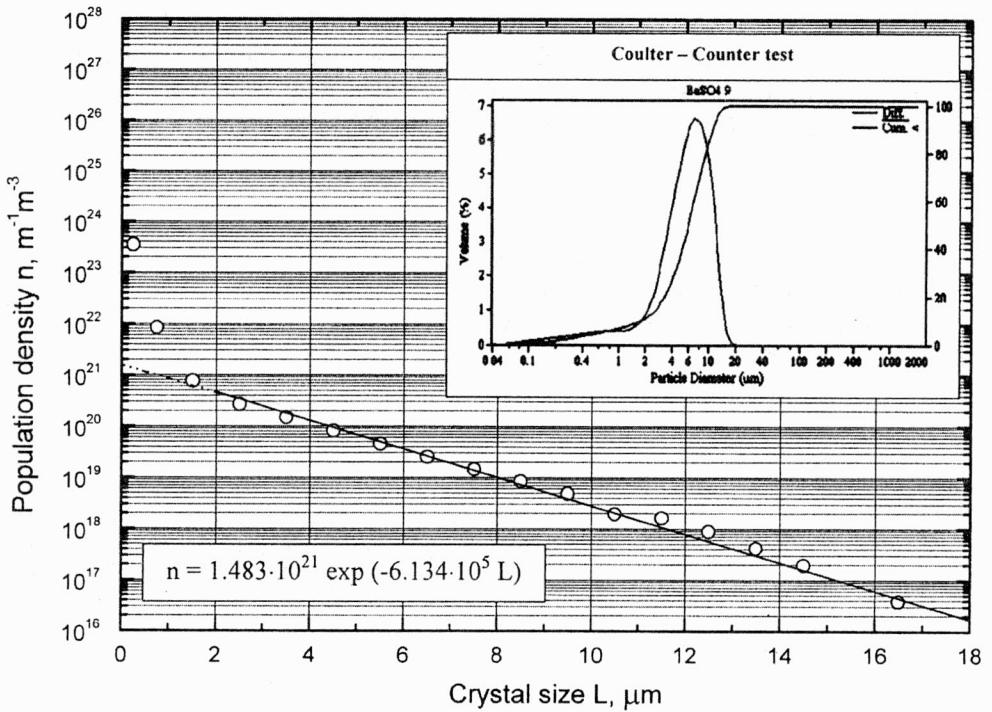

Fig. 3. Crystal-size distribution of barium sulphate ($T = 348$ K, $\tau = 3600$ s).
Concentration of barium chloride in feeding solution: 24.0 mass % ($M_T = 291.2$ kg BaSO$_4$/m^3).
The Coulter–Counter test: $L_m = 6.23$ μm, $L_{50} = 5.97$ mm, $CV = 55.0\%$.
Crystal growth rate of BaSO$_4$: $G_{rc} = 4.5 \cdot 10^{-10}$ m/s

At the temperature $T = 348$ K, when the crystallizer is fed with barium chloride solution of a concentration of 24.0 mass % ($M_T = 291.2$ kg BaSO$_4$/m^3), barium sulphate nucleation rate can be represented by the following equation [18]:

$$B_{rc} = 8.4 \cdot 10^{18} \tau^{-2.0} \tag{3}$$

and its crystal growth rate:

$$G_{rc} = 1.2 \cdot 10^{-7} \tau^{-0.68} \tag{4}$$

for the residence time $900 < \tau < 9000$ s.

The mean residence time τ and the supersaturation Δc are strongly interrelated. The supersaturation decreases with the increase of the residence time. The nucleation B_{rc} and the growth rate G_{rc} decrease with the increase of the residence time τ. However, the decrease is not equal ($B_{rc} \sim \tau^{-2.0}$, eq. (3); $G_{rc} \sim \tau^{-0.68}$, eq. (4)). In the case of low and mean supersaturations (long residence time), crystal growth rate often increases with the supersaturation faster than nucleation rate, resulting in a coarser crystal product. When the supersaturation is high and very high (short residence time), the nucleation rate can be comparable to the growth rate, and the product obtained becomes finer.

The nucleation rate B and the crystal growth rate G can be expressed as the functions of the supersaturation Δc [17]:

$$B = k_b \Delta c^b \tag{5}$$

and

$$G = k_g \Delta c^g . \tag{6}$$

Assuming that the growth of barium sulphate crystals may be described by the parabolic law of growth rate ($g = 2$, equation (6)) [8], [19], the nucleation order b obtained from equations (3) and (4) [18] is 5.86 (compare the data according to [20] and [21]). This applies to continuous $BaSO_4$ precipitation process, where concentrated (24 mass %) $BaCl_2$ solution ($c_{eq,\ 293\ K} = 26.3$ mass % [17]) and crystalline $(NH_4)_2SO_4$ feed the crystallizer.

After solubilizing the post-quenching salts in water, calcium, sodium and potassium ions appear additionally in the feeding solution (table 1). Then crystalline ammonium sulphate is fed in the stoichiometric ratio in relation to the sum of barium and calcium ions (table 1). The influence of solution composition on a mean size of crystalline product is shown in figure 4. Measurements were carried out at the temperature $T = 348$ K and for the residence time $\tau = 900$ s.

The coarsest crystals of barium sulphate ($L_m = 7.8$ μm) were obtained when the crystallizer was fed with $BaCl_2$ solution of a concentration of 10 mass % ($M_T = 114.7$ kg $BaSO_4/m^3$, $z = 10.5$ mass %, $\varepsilon = 0.975$). Due to addition of the sodium, potassium and calcium chlorides the crystal size L_m decreases to 3.9, 3.8 and 3.2 μm, respectively, provided that their concentration is 12.0 mass % (figure 4) [22]. The presence
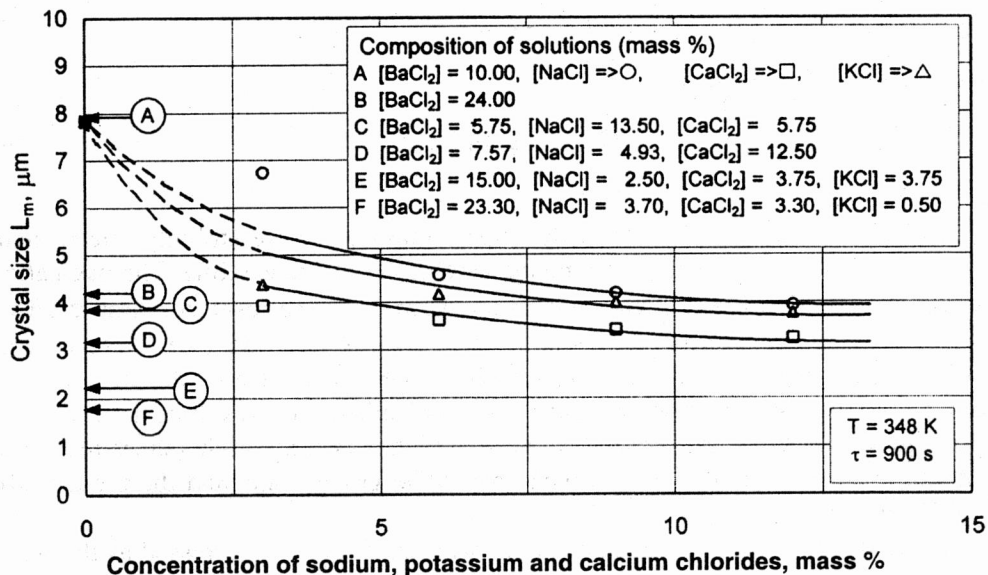
Fig. 4. The effect of feeding solution composition on crystalline product size

of sodium and potassium chlorides does not affect the crystal content in the suspension ($z = 10.5$ mass %, $\varepsilon = 0.974$), contrary to calcium chloride, which increases it considerably ($[CaCl_2] = 12.0$ mass %: $z = 19.3$ mass %, $\varepsilon = 0.930$). Additionally calcium sulphate(VI) ($CaSO_4 \cdot 2H_2O$) appears in the solid phase in the amount ranging from 11.5 mass % ($[CaCl_2] = 3.0$ mass %) up to 52 mass % ($[CaCl_2] = 12.0$ mass %). It is worth emphasizing that the crystal size in the $BaSO_4$ and $CaSO_4 \cdot 2H_2O$ mixture is small ($L_m = 3-4$ µm). Under comparable conditions ($T = 348$ K, $\tau = 900$ s) when the crystallizer is fed only with calcium chloride solution, coarser crystals of $CaSO_4 \cdot 2H_2O$ precipitate: $L_m = 232.7$ µm ($[CaCl_2] = 10.0$ mass %: $z = 13.0$ mass %, $\varepsilon = 0.939$) and $L_m = 114.7$ µm ($[CaCl_2] = 24.0$ mass %, $z = 28.0$ mass %, $\varepsilon = 0.849$).

Higher barium chloride concentration in the feeding solution ($[BaCl_2] = 24.0$ mass %) will obviously increase the number of barium sulphate crystals in a mixed suspension ($M_T = 291.2$ kg $BaSO_4/m^3$, $z = 23.3$ mass %, $\varepsilon = 0.935$) but simultaneously their sizes are smaller ($L_m = 4.3$ µm). This is becasue of an excessive nucleation in the reaction precipitation zone (inside the draft tube) caused by the way of feeding and mixing [14] and also by the physical form of reacting substances: concentrated barium chloride solution (and also other salts) – solid ammonium sulphate. It should be clearly emphasized that the concept of used quenching salts processing technology assumes full usage of the products obtained [12] (also mother liquid after barium ions precipitation). The concentrations of fertilizer compounds and microelements in the solution should be as high as possible. It is also advantageous to enrich the so-
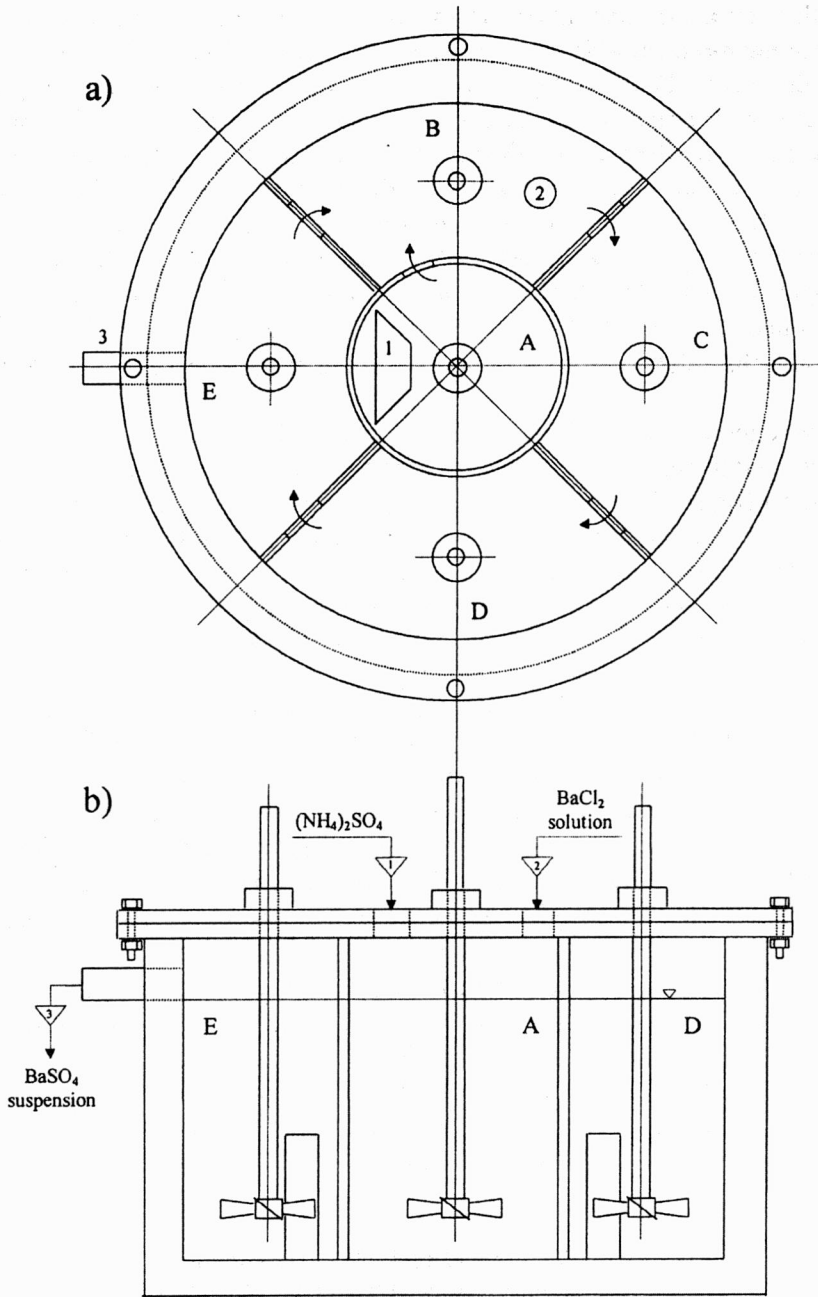
Fig. 5. Diagram of the crystallizer for barium sulphate precipitation (a – top view, b – section):
A, B, C, D, E – crystallizer chambers, 1 – crystalline ammonium sulphate input,
2 – barium chloride solution input, 3 – product suspension offtake

lution with ammonium ions (after barium sulphate precipitation from the solution B (figure 4) ammonium chloride concentration will reach 13.96 mass %).

The solutions C, D and E (figure 4) obtained after dissolution of used quenching salts in water were prepared in such a way as to achieve summary concentration of all their components on the level of 25 mass % (practically the solutions being saturated at the temperature approaching 293 K). Precipitation of barium sulphate from these solutions confirmed a disadvantageous influence of mainly barium chloride, but also other chlorides on crystal size of the product. An adverse effect of solid phase content in the suspension was also observed. When the crystallizer was fed with the solution C it was found that $\varepsilon = 0.964$, $L_m = 3.8$ μm, 55.2 mass % of $BaSO_4$ in the product, whereas with the solution E: $\varepsilon = 0.954$, $L_m = 2.2$ μm, 91.4 mass % of $BaSO_4$ in the product.

The above results were verified in the model scale. The tests were carried out in the continuous crystallizer of working capacity of 5.86 dm^3 ($V_t = 8.75$ dm^3, $D = 260$ mm, $H = 145$ mm) (figure 5). The crystallizer was divided into five chambers: cylindrical central chamber of an inside diameter of 100 mm and a working capacity of 0.86 dm^3, and four identical external chambers arranged around, whose sections formed a developed side surface of a truncated cone (working capacity of a chamber of 1.25 dm^3). Each of the crystallizer chambers is equipped with a four-paddle propeller agitator. The agitators with speed control forced intensive vertical circulation of suspension inside the chambers and the flow between the chambers. They also ensured a fast equalization of both temperature and concentration of components in the reaction mixture and during nucleation and growth of barium sulphate crystals [23]. The constant temperature in the crystallizer was kept by a 1000 W thermostatic heating system. Barium sulphate was precipitated from the solution obtained after solubilization of the waste A (table 1) in water. In such a way, the crystals of a size $L_m = 4.0$ μm ($T = 349$ K, $\tau = 7200$ s) were obtained from the solution that contained 7 mass % of $BaCl_2$ [24].

Crystals of a mean size of about 2 μm were obtained from the solution F (figure 4). At the temperature exceeding 323 K the concentration of soluble components of used quenching salt (A) in this solution (table 1) reached its maximum. Similar results were obtained in the pilot scale, where 10 Mg of this waste was processed. The installation was working continuously. Mean size of the barium sulphate crystals obtained was: $L_m = 2.6$ μm ($T = 348$ K, $\tau = 7200$ s).

3. PRODUCTS OBTAINED DURING USED QUENCHING SALTS' TREATMENT

The results of laboratory tests, model testing and technical data obtained experimentally and available in scientific literature were used to design and construct a pilot

USED QUENCHING SALT	
Barium chloride	56.5
Calcium chloride	10.1
Sodium chloride	9.0
Moisture	8.0
Others	16.4

UTILIZATION

FERTILIZER BASING SOLUTION			
N	4.4	Fe	0.00004
Na	3.2	Cd	<0.00001
K	0.38	Cr	<0.00001
B	0.04	As	<0.00001
Zn	0.06	Pb	<0.0001
Mn	0.0003	Sr	<0.0001
Mg	0.00007	Ti	<0.00001
Cu	0.003	V	<0.00001
Mo	0.017		

Fertilizer components

(urea, potassium chloride, magnesium, manganese, cupric, zinc and ferric sulphates, ammonium molybdate and others)

	FERTILIZER A	FERTILIZER B
pH	6.0	5.8
Density	1270 kg/m^3	1300 kg/m^3
N	5.0	8.0
K	6.0	4.0
Mg	2.0	1.6
B	0.02	0.018
Cu	0.6	0.6
Mn	0.8	0.8
Na	0.7	0.6
Mo	0.0004	0.004
Fe	–	0.8
Zn	–	0.6

BARIUM SULPHATE	
Ca	3.970
B	0.133
Sr	0.027
Mn	0.021
Cu	<0.0001
Fe	<0.006
BaSO4	≤93.0
Graining	≤15 μm

Production of barium salts Glass–making industry and others

SOLID WASTE	
Fe	38.534
Ca	6.687
Al	1.842
Mg	0.548
Mo	0.531
Sr	0.370
Cr	0.438
Na	0.229
Cu	0.139
Ni	0.124
Zn	0.078
Ti	0.054
Mn	0.020
Pb	0.020
B	0.015
K	0.004
Cd	0.004
BaSO$_4$	5.9

Building materials

► **Liquid fertilizer for grassland**
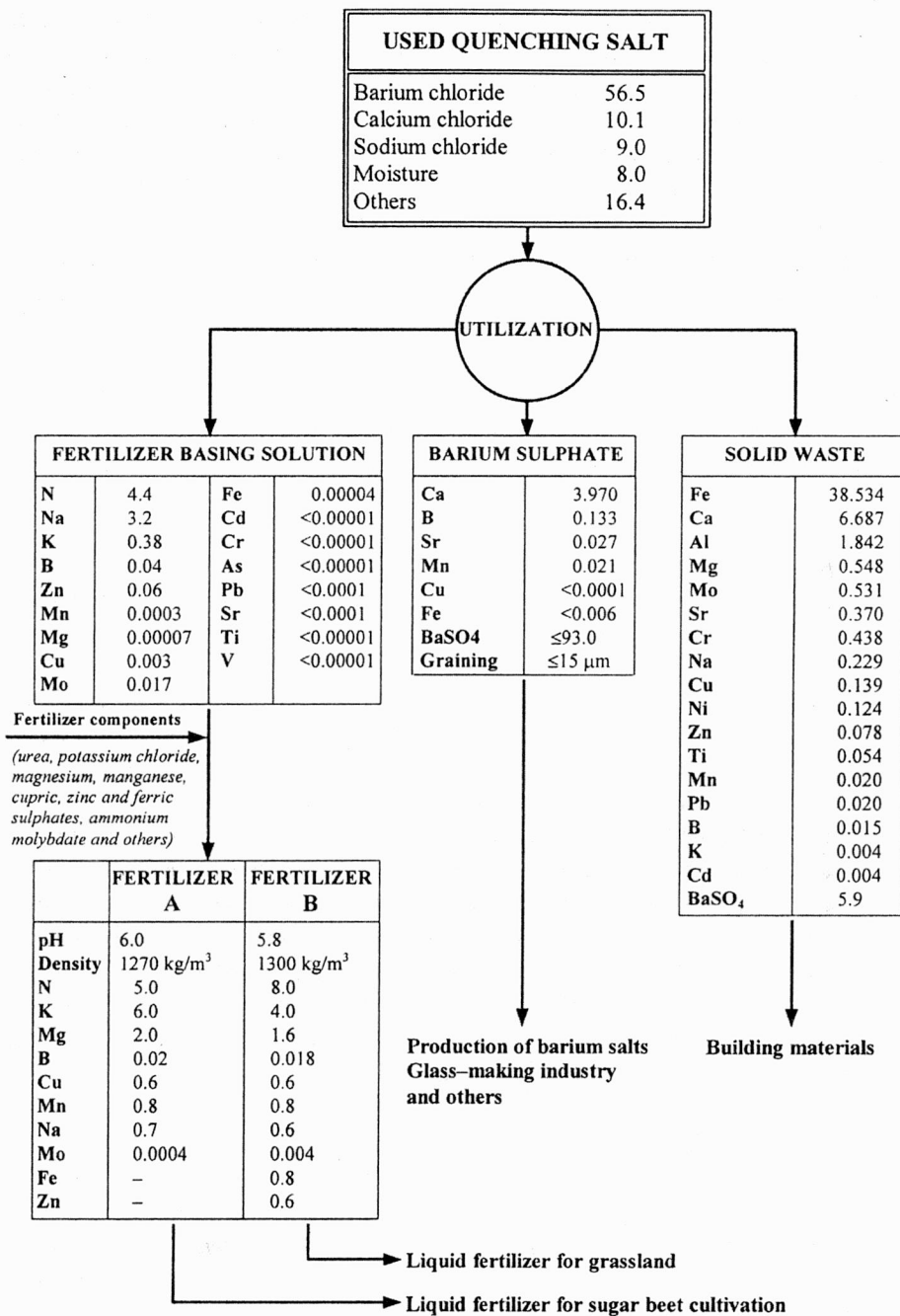
► **Liquid fertilizer for sugar beet cultivation**

Fig. 6. Example compositions (in mass %) of raw materials and products in the technology of used quenching salts processing

installation, where 10 Mg of used quenching salt were processed (the waste A, table 1) [7]. Barium sulphate was precipitated by crystalline ammonium sulphate (95.6 mass % of $(NH_4)_2SO_4$) in the crystallizer with the mixed suspension of the working capacity of 1.2 m^3. Barium sulphate [25] and liquid mineral fertilizers [26] were the products obtained. From the used quenching salt, whose composition is given in figure 6, the product comprising 86.2 mass % of barium sulphate, 13.4 mass % of calcium sulphate and 0.4 mass % of impurities was precipitated. Barium sulphate crystals of a mean size ranging from 2 to 5 μm were obtained (maximal crystal size of ca. 15 μm). The solution being used for mineral fertilizers production is the ammonium chloride solution (16.8 mass % of NH_4Cl) containing macro- (potassium ions) and micronutrients (figure 6).

The chemical composition of barium sulphate is strictly connected with the composition and physical form of used quenching salt, therefore with its solubilization in water. Chemical purity of the product is considerably influenced by calcium ion concentration in the solution. Calcium chloride content in used quenching salts may reach even 50 mass % (in one of used quenching salts investigated, calcium ions constitute 16.6 mass %, which corresponds with 44.47 mass % of $CaCl_2$ in the waste C, table 1). Because of its very good solubility in water (42.7 mass % in 293 K, 58.6 mass % in 343 K [17]) practically all calcium ions pass to water and then are precipitated by ammonium sulphate (solubility in the $NH_4Cl–CaSO_4–H_2O$ system [27]). Therefore the product must consist of the mixture of both sulphates: barium sulphate and calcium sulphate. This reduces its market value and suitability [28]. Nevertheless it may be recommended as a semi-finished product for a valuable compound – barium carbonate, which may be converted into other barium salts [29]–[31].

The solution obtained after precipitation of barium ions and some amount of calcium and other metal ions practically do not contain heavy metal ions. Therefore it is a suitable semi-finished product for the production of multicomponent liquid mineral fertilizers [26]. Ammonium (16.8 mass %), sodium (8.1 mass %) and potassium (0.7 mass %) chlorides are the main components of this solution. Relatively high content of sodium ions (3.2 mass %) in this solution limits its agricultural applications [12]. Such concentration of sodium is required for a proper growth of some plants only, i.e. sugar beet and grassland. Taking this into account two mineral fertilizers were prepared (figure 6):

• for sugar beet – liquid, clear, of the following formula N:K:Mg = 1:0.5:0.4,
• for grassland – liquid, clear, of the following formula N:K:Mg = 1:0.5:0.2.

Agricultural suitability of the prepared samples of fertilizers was assessed on the basis of biological tests with cuckoo flower (*Cardamine pratensis* L.) in laboratory conditions (seed germination test) [32]. Application of both fertilizers showed their beneficial effect on seed germination and plant growth [12].

Solid wastes obtained during used quenching salts processing were tested in laboratory for the possibility of their further utilization. Elution tests on the solutions

simulating extreme environmental conditions were carried out according to the recommendations of American Standard Association [33], [34]. The waste (5 mass %) was added to a concrete mix. Elution tests were completed after 48 hours and the concentrations of metals in elution liquids were determined [12]. It was found that the concentrations did not exceed the highest admissible values for impurities in wastewater introduced to the ground and water [4].

4. A NEW INSTALLATION FOR PROCESSING OF USED QUENCHING SALTS

The installation throughput was proposed to be 130 Mg of waste per year [35]. It was assumed that this semi-continuous system worked under atmospheric pressure. The processing procedure was arranged in the following successive steps: drying, metal parts removal and used quenching salt isolation, solubilization in water, suspension separation, insoluble residue utilization (solid waste), barium sulphate

Table 2

Characteristics of barium sulphate precipitation and crystallization
in an exemplary system for processing used quenching salt

Parameters and devices	Unit of measure	Value
Temperature	K	348
Crystallization time	h	2–4
Concentration of $BaCl_2$ in the feed solution	mass %	23.3
Solid phase content in the suspension	mass %	25.3
Concentration of NH_4Cl in the solution	mass %	16.8
Content of $BaSO_4$ in the solid phase	mass %	86.2
Crystallizer with agitator		
Cylindrical tank with ellipsoidal bottom and flat cover		
– total capacity		
– working capacity	m^3	1.48
– diameter	m^3	1.14
– total height	mm	1200
Three-blade propeller agitator	mm	1600
– diameter		
– distance from bottom	mm	300
– number of agitation per second*	mm	400
– motor rating	r.p.s.	10
Heat requirement	kW	5.2
Heating steam consumption (at 300 kPa)	MJ	240
	kg/m^3 of solution	100

* The agitation speed may be regulated from 4 to 20 r.p.s., depending on a device: mixer for solubilization of used quenching salt or barium sulphate crystallizer.
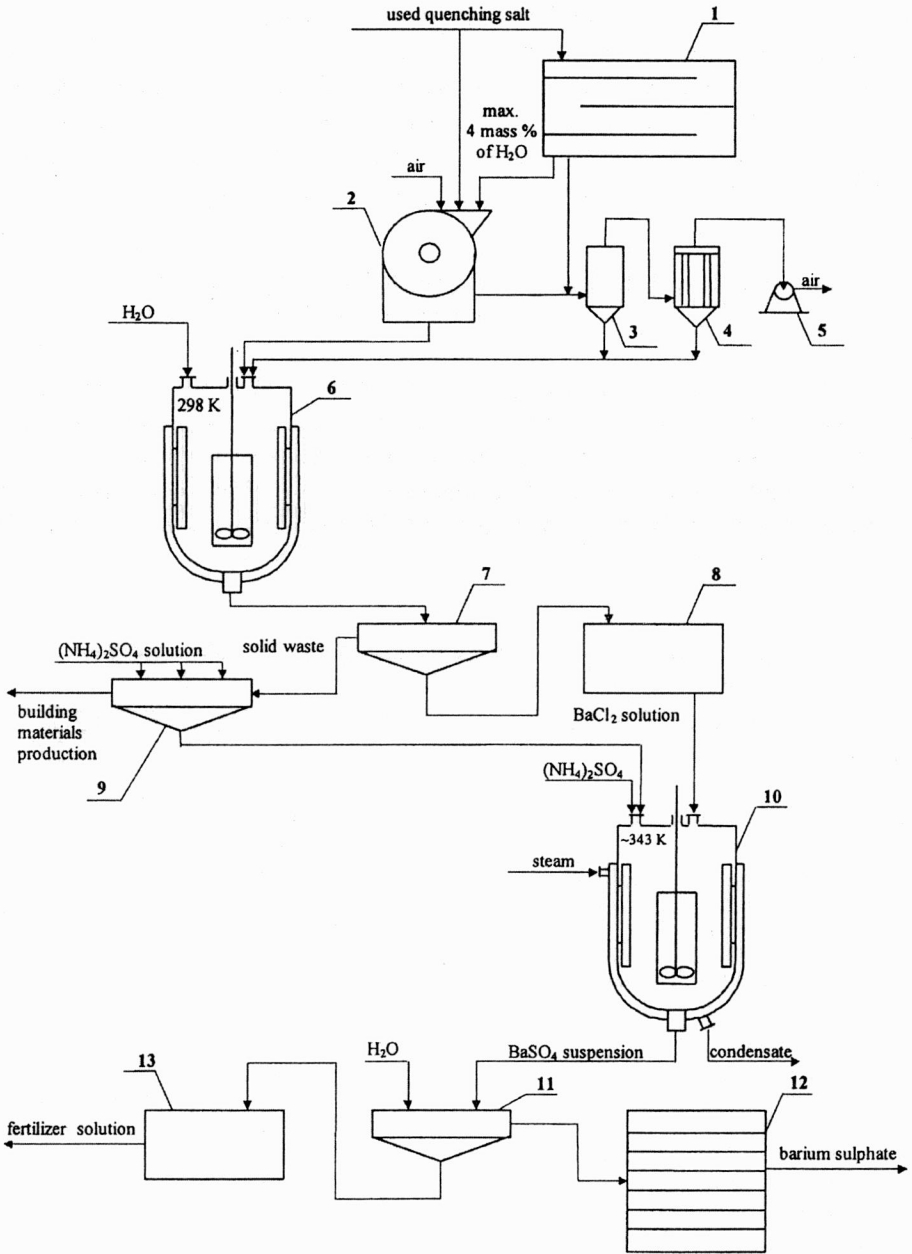
Fig. 7. Simplified diagram of the system for used quenching salts processing: 1 – dryer, 2 – hammer mill, 3 – cyclone, 4 – bag filter, 5 – blower, 6 – mixer, 7 – vacuum nutsche filter, 8 – barium chloride solution tank, 9 – nutsche filter, 10 – barium sulphate crystallizer, 11 – filter, 12 – chamber dryer, 13 – fertilizer basing solution tank

precipitation by crystalline ammonium sulphate(VI) and crystallization, filtration, filtrate utilization (solution for liquid mineral fertilizers' production), washing and drying of crystal product (barium sulphate). One charge per day enables us to process 525 kg waste/day (24 h), with the average content of the main components as given in figure 6. The other raw materials are technical ammonium sulphate and water. Figure 7 shows simplified diagram of the system for used quenching salts processing.

The used quenching salt in the form of lumps of various sizes is temporarily stored in receptacles (e.g. metal containers). From each of the receptacles a final salt sample is taken and the moisture as well as barium, calcium, sodium and potassium chlorides content are determined. It is recommended to conduct laboratory tests of salt solubility and to determine the concentrations of two basic components, i.e. barium chloride and calcium chloride, in the solution. The minimum volume of water indispensable for solubilizing a definite waste and the minimum quantity of ammonium sulphate necessary for precipitating barium ions (and also calcium ions) are calculated on this basis. If the moisture content in the used quenching salt exceeds 4 mass %, drying is necessary (e.g. in a belt dryer).

The system is equipped with plain and typical apparatuses and devices. Because the system operates in a semi-continuous way it is possible to use the same apparatus or device during different processes [35].

Table 2 gives basic parameters of the barium sulphate precipitation process.

It should be firmly stressed that the results in table 2 and figure 6 describe the processing of 525 kg (1 charge) of used quenching salt of specific chemical composition per day (24 h). Different waste composition (table 1) is equivalent to different values of raw material consumption factors, different chemical compositions of the products obtained and different composition of fertilizer additives.

5. CONCLUSIONS

The system designed allows processing of a very toxic waste, used quenching salts, in such a way as to obtain two usable products: barium sulphate and solution for production of liquid mineral fertilizers. By-product is a solid waste, practically devoid of barium ions. The process is based on controlled solubilization of quenching waste in water and subsequent precipitation of barium ions using crystalline ammonium sulphate.

In the $BaSO_4–NH_4Cl–H_2O$ system, the nucleation rate of barium sulphate may be calculated from equation (3), and the crystal growth rate – from equations (1) and (4). Crystal size of the product obtained depends on precipitation and crystallization temperature, barium ions' concentration in the feeding solution and residence time (equation (2), figure 2).

When barium chloride concentration in the solution is constant (10.0 mass %), the presence of sodium, potassium and calcium chlorides decreases a mean size of $BaSO_4$ crystals from 7.8 μm to 3.9, 3.8 and 3.2 μm, respectively (at the concentration of each

chloride of 12.0 mass %). Higher content of crystals in the mixed suspension influences disadvantageously their size ([BaCl$_2$] = 10.0 mass %: L_m = 7.8 µm when ε = 0.975; [BaCl$_2$] = 24.0 mass %: L_m = 4.3 µm when ε = 0.935). Due to presence of calcium chloride the mixture of BaSO$_4$ and CaSO$_4$·2H$_2$O appears in a solid phase. Mean size of their crystals is small (L_m ranges from 3 to 4 µm). From the solutions obtained after solubilization of used quenching salts in water small crystals of BaSO$_4$ and CaSO$_4$·2H$_2$O mixture are precipitated under similar conditions (T = 348 K, τ = 900 s, chlorides concentration of 25–30 mass %). Mean size of their crystals was about 2 µm.

Depending on the composition of the waste (table 1) and its physical form, and hence on the degree of its solubilization in water, barium sulphate may contain from 3 to 12 or more mass % of pollutants. These pollutants are mainly the compounds of calcium, strontium and manganese and, to a smaller extent, of iron and copper (figure 6). Crystals of barium sulphate of an average size of 2–5 µm are obtained (maximum grain diameter approaches 15 µm). It is recommended as a semi-finished product for obtaining a valuable compound, i.e. barium carbonate, which may be converted into other barium salts, and also as a product for glass industry.

The solution obtained after solubilization of used quenching salts in water and precipitation of barium ions (and also a certain quantity of calcium and other metal ions) practically does not contain any heavy metal ions. On the other hand, it contains micro- and macronutrients (figure 6). It is therefore perfectly suitable as an intermediate product for obtaining multi-component liquid mineral fertilizers. After supplementing the solution with the components required, fertilizer can be used for additional leaf and root plants nourishment through the whole period of vegetation. Due to a high content of sodium in this solution, two fertilizers were prepared: for sugar beet and for grassland, the cultivation of which requires such quantities of this element. Agricultural suitability of the prepared samples of fertilizers was assessed on the basis of biological tests with cuckoo flower (*Cardamine pratensis* L.) in laboratory conditions (seed germination test). Both fertilizers applied in a dose of 200 and 400 kg N/ha advantageously influenced germination of seeds and plant growth.

The proposed technology of used quenching salts processing is practically waste-free. Even the solid waste, devoid of barium ions, may be utilized. The trials of solidification of the solid waste obtained by means of cement and utilizing the solidification product for production of small size building elements were found satisfactory.

The technological system designed and described above was successfully verified on an experimental production scale and proved to be a definite implementation offer.

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UTYLIZACJA SOLI POHARTOWNICZYCH

Zaprojektowano i przetestowano instalację do przerobu soli pohartowniczych. Istotą opracowanej technologii jest wydzielenie siarczanu baru z roztworu powstałego po roztworzeniu w wodzie soli pohartowniczych przez dodanie stałego siarczanu amonu. Umożliwia to przerób tych soli na dwa użyteczne produkty: siarczan baru i roztwór do produkcji ciekłych nawozów mineralnych oraz praktycznie nieszkodliwy odpad, który może być wykorzystany do produkcji materiałów budowlanych. Zaprojektowano i wykonano instalację doświadczalno-produkcyjną, w której przetworzono 10 Mg odpadu pohartowniczego zawierającego około 60% mas. $BaCl_2$. Scharakteryzowano parametry pracy instalacji oraz omówiono właściwości otrzymanych produktów: siarczanu baru, roztworu nawozowego i odpadu stałego. Określono wpływ temperatury, czasu przebywania oraz stężeń chlorków: baru, wapnia, sodu i potasu w roztworze zasilającym krystalizator na szybkość wzrostu i wielkość kryształów siarczanu baru.