



## BENEFICIATION AND PROCESSING OF NATURAL AND TECHNOGENIC RAW MATERIALS

Research paper

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**Effect of sonochemical pretreatment of slurry depressors on sylvite flotation performance**V. E. Burov<sup>1</sup> , V. Z. Poilov<sup>1</sup> , Z. Huang<sup>2</sup> , A. V. Chernyshev<sup>1</sup>, K. G. Kuzminykh<sup>1</sup> <sup>1</sup> Perm National Research Polytechnic University, Perm, Russian Federation<sup>2</sup> Jiangxi University of Science and Technology, Guanzhou, China

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**Abstract**

The main source of potassium fertilizers is sylvite ores consisting primarily of halite (NaCl), silicate and clay-carbonate slurries (clay-salt slurries). Processing of natural potash ores is mainly carried out by the flotation method, which separates KCl, NaCl, and clay-salt slurry. The research is aimed at revealing the effect of sonochemical pretreatment of the depressor reagents, CMC and starch, on dynamic viscosity, aggregate size, electrokinetic potential of these reagent solutions and sylvite flotation performance. It has been established that sonochemical treatment of depressor solutions decreases the size of aggregates of starch molecules by more than 133 times and that of aggregates of CMC molecules from 6 to 4 nm. It has been revealed that sonochemical treatment of anionic CMC solution shifts the electrokinetic potential towards the area of negative values with an increase in acoustic power, while sonochemical treatment of any acoustic power has no effect on the zeta potential of nonionic starch. It has been found that the sonochemical treatment lowers the dynamic viscosity of CMC and starch solutions: the viscosity of CMC solution at a maximum acoustic power of 420 W decreases by 44 % and the viscosity of starch solution at the same acoustic (ultrasonic) power decreases by 70 %. Furthermore, sonochemical pretreatment of sylvite flotation depressors contributes to an increase in KCl recovery and a decrease in the slurry content in the flotation concentrate. The possibility of reducing the consumption of ultrasonic treated depressor is also demonstrated. It is expedient to test the obtained findings in pilot-plant conditions.

**Keywords**

processing, sylvite flotation, ultrasound, depressor, clay-salt slurry, carboxymethylcellulose, starch, zeta potential, dynamic viscosity, recovery

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## ОБОГАЩЕНИЕ, ПЕРЕРАБОТКА МИНЕРАЛЬНОГО И ТЕХНОГЕННОГО СЫРЬЯ

Научная статья

**Влияние предварительной сонохимической обработки депрессоров шламов на эффективность сальвинитовой флотации**В.Е. Буров<sup>1</sup> , В.З. Пойлов<sup>1</sup> , Ч. Хуан<sup>2</sup> , А.В. Чернышев<sup>1</sup>, К.Г. Кузьминых<sup>1</sup> <sup>1</sup> Пермский национальный исследовательский политехнический университет, г. Пермь, Российская Федерация<sup>2</sup> Университет науки и технологии Цзянси, г.о. Ганьжоу, Китай

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**Аннотация**

Основной источник калийных удобрений – сальвинитовые руды, состоящие в том числе из галита (NaCl), силикатных и глинисто-карбонатных шламов (глинисто-солевых шламов). Обогащение природных калийных руд главным образом осуществляется флотационным методом, при котором происходит разделение KCl, NaCl и глинисто-солевых шламов.

Исследование направлено на выявление влияния предварительной сонохимической обработки реагентов-депрессоров – КМЦ и крахмала – на динамическую вязкость, размер агрегатов, электрокине-



ческий потенциал растворов этих реагентов и на эффективность сальвиновой флотации. Установлено, что сонохимическая обработка растворов депрессоров уменьшает размер агрегатов молекул крахмала более чем в 133 раза, агрегатов молекул КМЦ – с 6 до 4 нм. Выявлено, что сонохимическое воздействие на раствор анионного КМЦ с увеличением акустической мощности смещает электрокинетический потенциал в область отрицательных значений, при этом сонохимическая обработка любой акустической мощности не влияет на дзета-потенциал неионогенного крахмала. Установлено, что сонохимическая обработка понижает динамическую вязкость растворов КМЦ и крахмала: вязкость раствора КМЦ при максимальной акустической мощности 420 Вт снижается на 44 %, вязкость раствора крахмала при той же акустической мощности ультразвука – на 70 %. Кроме того, предварительная сонохимическая обработка депрессоров сальвиновой флотации способствует увеличению извлечения КС1 и снижению содержания шламов во флотационном концентрате. Также показана возможность снижения расхода обработанного ультразвуком депрессора. Полученные результаты целесообразно апробировать в опытно-промышленных условиях.

#### Ключевые слова

обогащение, сальвиновая флотация, ультразвук, депрессор, глинисто-солевой шлам, карбоксиметил-целлюлоза, крахмал, дзета-потенциал, динамическая вязкость, извлечение

#### Для цитирования

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### Introduction

Potassium, along with phosphorus and nitrogen, is the most important component of mineral fertilizers, which enhances the yield of agricultural plants [1–4]. The main source of potash fertilizer is sylvite ore, which consist of halite (NaCl), silicate and clay-carbonate slurries (clay-salt slurries; herein-after – CSS) [4, 5]. Beneficiation of natural potash ores is mainly carried out by the flotation method, which separates KCl, NaCl, and CSS [6–8].

Russia hosts one of the world's largest sylvite ore deposits, the Verkhnekamskoe potassium-magnesium salt deposit, which is rich in valuable sylvite [9, 10]. To date, however, some of the best sylvite ore lodes (layers) have already been mined-out at the deposit, and therefore the layers with lower content of sylvite and with a higher content of CSS are increasingly being used. This leads to the deterioration of the ore processing performance [11, 12]. At the same time, the clay-salt minerals ( $\text{CaSO}_4$ ,  $\text{MgCO}_3$ ,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaMg}(\text{CO}_3)_2$ ,  $\text{F}^-$ ,  $\text{MgCl}_2$ ), which have a greater cation exchange capacity to the salts of primary aliphatic amines used as sylvite flotation collecting agents, produce the greatest adverse impact on the KCl flotation [6, 11, 13, 14]. Competing adsorption of amines on CSS prevents their adsorption on the crystals of potassium chloride that leads to the deterioration or termination of the flotation process [12, 15].

To reduce the CSS content in the ore, mechanical or flotation deslurrying of potassium ores is used prior to the sylvite flotation [12]. However, such methods are incapable of removing CSS completely. Even tenths of percent of clay-salt impurities

remaining in the ore decrease the recovery of potassium chloride to the flotation concentrate and also require additional consumption of collecting agents (aliphatic amines) [16, 17]. In this regard, at the stage of sylvite flotation prior to entering collecting agents into the process, ore pulp is conditioned by depressors, which are adsorbed on the surface of CSS, change the nature of the interphase molecular interactions, thus increasing the selectivity of flotation. As a result, recovery of KCl increases, content of CSS in the flotation concentrate decreases, with reducing consumption of collecting agents [8, 11, 12, 18, 19].

A large number of depressing agents (depressors) for flotation of potassium ores is known, of which organic agents should be noted: carboxymethylcellulose (CMC), modified urea-formaldehyde resins, modified starch, guar gum, epoxy resin, etc. [11, 12, 18]. These chemical compounds have proven to be effective CSS depressors. However, organic depressor molecules (e.g., CMC and starch) in solutions tend to form associates and supramolecular structures, the formation of which is promoted by increasing the agent concentration. Besides, ionogenic polymers, in particular CMC, are also characterized by the globulization of molecules and an increased intramolecular interaction [20–22]. As the concentration of organic depressor solutions increases, the viscosity of the solution increases and simultaneously the depressor properties deteriorate [21]. Therefore, commercial operations seek to use dilute solutions of depressors (e.g.,  $\text{CMC} < 2\%$ ), which can increase the depressing effect of the agents and reduce their specific consumption. How-

ever, the use of dilute depressor solutions leads to an additional introduction of water into the process, which causes losses of potassium chloride due to dissolution and accumulation of excessive alkali liquors.

Sonochemical pretreatment of highly concentrated organic depressor solutions is a promising way of solving the aforementioned problems [23]. Under the effect of ultrasonic cavitation, various physicochemical properties of colloidal system, such as viscosity, size of depressor molecules aggregates, electrokinetic potential, the adsorption value of depressor molecules on clay-salt impurities change, which, in turn, can increase the performance of flotation of potash ores [24, 25]. In the literary sources, there is practically no information concerning the effect of ultrasonic pretreatment of depressors on both the physicochemical properties of a depressor and on the flotation performance of a sylvinite ore.

The purpose of this study is to establish the effect of sonochemical pretreatment of depressors (CMC and starch) on the physicochemical properties of the depressor solutions, as well as on the performance of sylvinite flotation.

## 1. Research Materials and Methods

### 1.1. Flotation depressor (depressing agent)

Two types of organic depressors, carboxymethyl cellulose (degree of polymerization of 750–850) and soluble starch amyloextrin (C.P.) (hereinafter – starch) were used to study the effect of sonochemical treatment on a depressor in sylvin flotation. For the tests, 4 % aqueous solution of CMC and 4 % aqueous

solution of starch were prepared at the solution temperatures of 30 °C.

In the process of sylvinite ore flotation beneficiation the depressor was added to the pulp before adding the emulsion of collector and frothing agent at the stage of sylvinite flotation. At the same time the specific consumption of CMC was 400 g/t ore, that of starch, 160 g/t ore [11].

### 1.2. Sonochemical treatment of depressor solution

Sonochemical treatment of the depressor solution was carried out using the ultrasonic unit shown in Fig. 1. As a source of ultrasonic vibrations, UZTA-0,8/22-OMU (series “Wave”) ultrasonic generator with piezoelectric oscillating system with developed radiating surface (made of titanium alloy) in the metal case and with forced air cooling was used.

The installation has a nominal operating frequency of  $22 \pm 1.65$  kHz and the intensity of radiation not less than  $3.5 \text{ W/cm}^2$ . Electronic generator with timer and power regulator (40–100 %). At an ultrasonic impact at 100 % power, the total power consumption is 1600 VA, the active power input is 650 W, providing acting acoustic power of about 420 W. The depressor solution temperature was maintained by thermostat 3. A depressor solution in an amount of 500 ml was placed into reactor 4, then treated by ultrasound at different levels of acoustic power (from 168 to 420 W in increments of 84) and exposure duration of 150 s. For comparison, control tests without sonochemical treatment under identical conditions were performed.

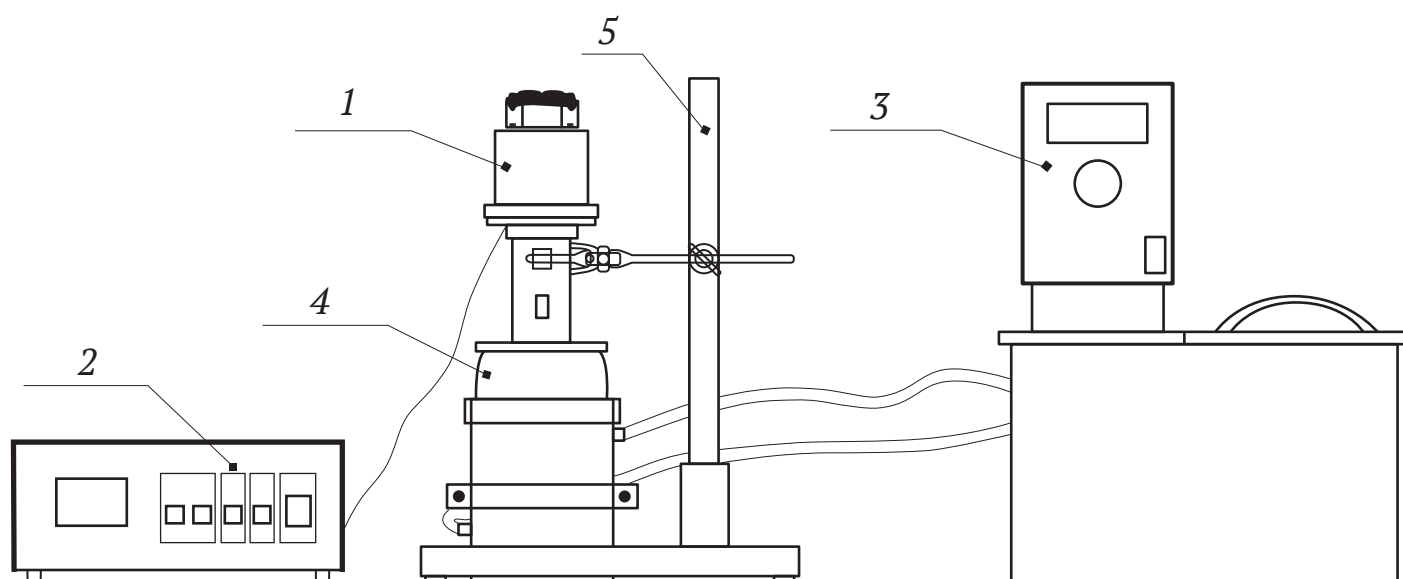


Fig. 1. Schematic representation of laboratory installation for sonochemical treatment of depressing agent: 1 – radiating element; 2 – ultrasonic generator; 3 – thermostat; 4 – reactor with a jacket; 5 – tripod



### 1.3. Measurement of aggregate size and zeta potential of depressor solution

The aggregate size and zeta potential of CMC and starch depressors were measured by a Zetasizer Nano ZS laser instrument using the dynamic light scattering method with non-invasive backscattering technique. The viscosity values used to measure the aggregate size and zeta potential were taken equal to the reference values of water viscosity at a given temperature. The refractive index of the CMC solution is 1.515; that of the starch solution is 1.340.

Ten measurements of aggregate size in a sample volume were taken sequentially by the instrument, and then the results were averaged. There were three parallel measurements per sample.

### 1.4. Measurement of viscosity-temperature properties of the depressor solution

The dynamic viscosity of the ultrasonically treated and untreated depressor solutions was determined with an SV-10 AND vibro-viscosimeter. The technique for determining viscosity is based on changing the resonance frequency of oscillations in a liquid of different viscosity at a given known value of the solution density. The initial density of 4 % CMC solution at 30 °C was 1.02 kg/m<sup>3</sup>; that of 4 % starch solution at 30 °C was 1.01 kg/m<sup>3</sup>.

The solution temperature was measured by the vibro-viscosimeter's temperature sensors directly during the viscosity measurements. The temperature of the depressor solutions was changed using a laboratory thermostat.

The limit of tolerable relative error of the viscometer is  $\pm 3\%$ , the repeatability of viscosity measurement results, not more than 1 % (standard deviation).

### 1.5. Flotation tests

Dry sylvinitic ore from flotation plant BKPRU-3 and sylvinitic flotation feed (deslurried sylvinitic ore) originating from flotation plant SKRU-3 of PJSC "Uralkali" of various chemical compositions (see Table 1) were used as raw materials for flotation production of potassium chloride in the tests.

Potassium chloride of "C.P." grade and sodium chloride of "C.P." grade were used for the prepara-

tion of saturated solutions used in the sylvinitic flotation study. The saturated solution was used only once.

Granulated primary amines (distilled) of C<sub>17</sub>–C<sub>20</sub> fraction and triethylene glycol C<sub>6</sub>H<sub>14</sub>O<sub>4</sub> were used as a collector and frothing agent for sylvinitic flotation, respectively. To prepare the amine hydrochloride solution, solid stearylamine (pre-milled) with a concentration of 0.8 wt. % was added to distilled water and chemically pure (C.P.) hydrochloric acid in the amount 15 % higher than necessary to neutralize the stearylamine. The resulting solution was stirred and thermostatted at 70 °C for 90 min. Then the agent temperature was reduced to working temperature of 60 °C. Then the frothing agent was added to the amine hydrochloride solution in the amount of 30 % by weight of the dry collector.

The flotation tests were carried out using a "FML 3/240 FL" laboratory flotation machine. Dry initial ore was mixed with mother liquor at a L/S phase ratio of 2.5. The resulting pulp (ore suspension) under stirring was firstly added with an ultrasound treated or untreated depressor at a given consumption of the agent, then conditioned for 3 minutes, and then added with the "collector-frother" composition at a consumption of 65 g/t of ore, and then conditioned again for 1 minute. The laboratory flotation machine's cell was filled with ready ore suspension in the volume of 500 ml (the ore mass of 194 g, the mother liquor volume of 400 ml). The flotation machine was switched on with the impeller rotation velocity of 29 RPS and the air flow rate of 100 l/h. The duration of the flotation process was 6 min (three flotation cycles were performed per sample, the results of which were averaged). The collected froth product and flotation tail were filtered with a vacuum filter, then dried to constant weight. After drying, gravimetric analysis of the obtained products and tails was carried out and the content of potassium chloride in the flotation concentrate and the flotation tails was determined using a PFA 378 flame photometer. The analysis for the content of CSS in the flotation concentrate was carried out using an EDX-8100P "Shimadzu" energy dispersive X-ray fluorescence spectrometer with helium sparging. Such elements as Ca, Si, Al, Mg, S, and Fe were referred to CSS.

Table 1

Chemical composition of sylvinitic ore originating from BKPRU-3 flotation plant and sylvinitic flotation feed from SKRU-3 flotation plant of PJSC "Uralkali"

Flotation plant	Weight percent of components, %					Fraction
	NaCl	KCl	Insol. res.*	MgCl <sub>2</sub>	CaSO <sub>4</sub>	
BKPRU-3	66.65	26.59	4.59	0.27	1.9	(–0.900 + 0.315) mm
SKRU-3	70.30	27.10	0.46	0.13	2.01	(–0.900 + 0.315) mm

\* Insol. res. – insoluble residue.



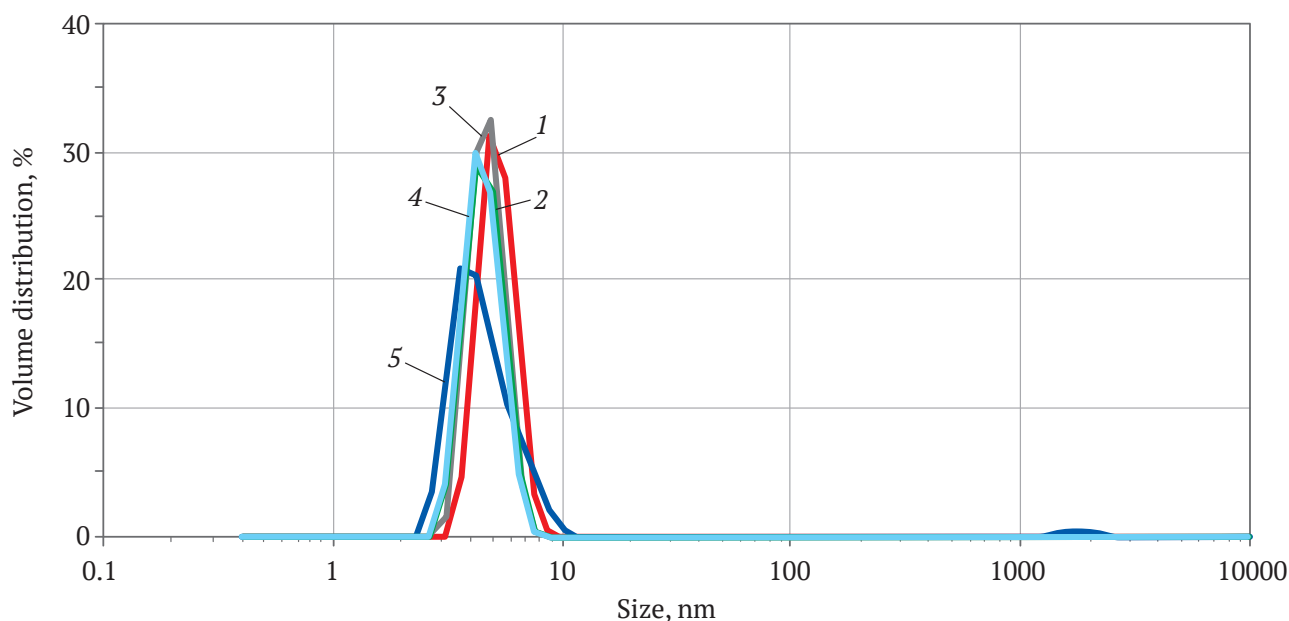
## 2. Findings Discussion

### 2.1. Influence of sonochemical treatment of depressor on aggregate size

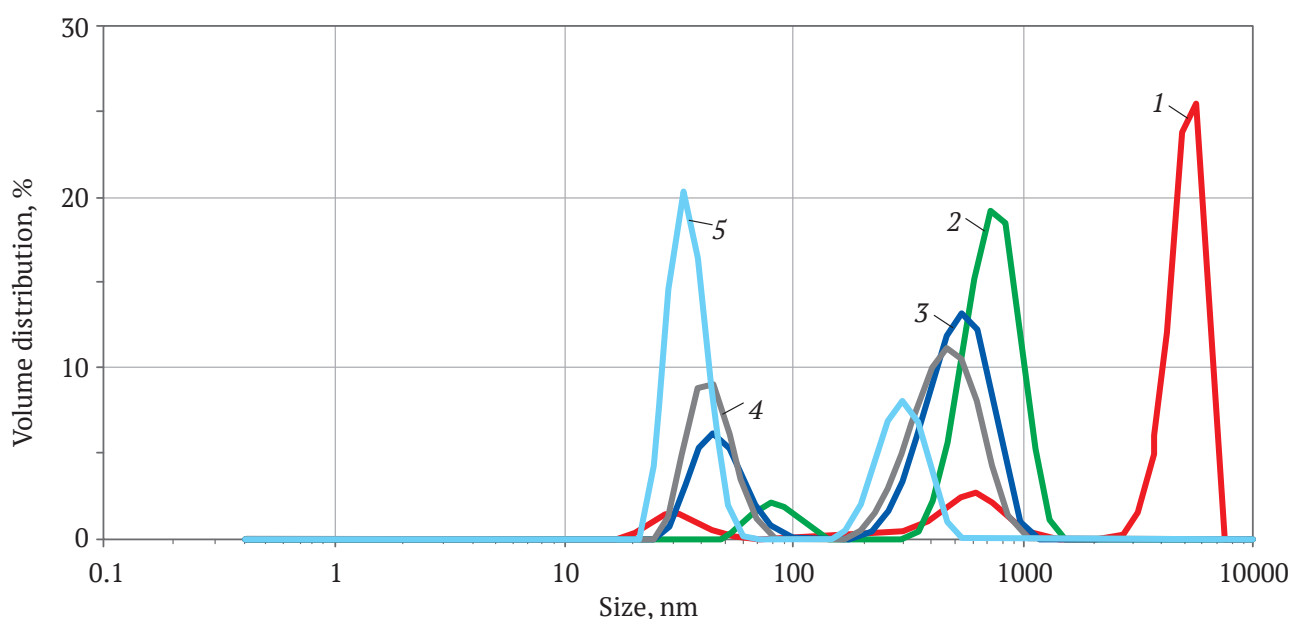
The results of the investigation of the effect of sonochemical treatment modes of depressor solutions on the size of aggregates (differential curves of the volume distribution of aggregates of CMC and starch molecules by size) are shown in Figs. 2 and 3.

As can be seen from Fig. 2, with increasing power of sonochemical influence the size of aggregates of molecules decreases: from 6 nm (without ultrasound treatment) to 4 nm (at acoustic power of ultrasound of 420 W). In concentrated solutions of CMC (above 1 %) exposed to ultrasound, breaking of bonds of macromolecules, which become loose and possess more expanded form, happens [26–28].

As can be seen from the analysis of the differential curves describing the volume distribution of starch



**Fig. 2.** Differential curves of volume distribution of aggregates of molecules in ultrasound-treated and non-treated CMC solution at duration of ultrasound exposure of 150 s:  
1 (red) – without ultrasonic treatment; 2 (green) – 168 W; 3 (gray) – 252 W; 4 (turquoise) – 336 W; 5 (blue) – 420 W



**Fig. 3.** Differential curves of volume distribution of aggregates of molecules in ultrasound-treated and non-treated starch solution at duration of ultrasound exposure of 150 s:  
1 (red) – without ultrasonic treatment; 2 (green) – 168 W; 3 (blue) – 252 W; 4 (gray) – 336 W; 5 (turquoise) – 420 W



molecules aggregates, presented in Fig. 3, large starch aggregates without sonochemical treatment had different sizes: about 50, 900, and 8000 nm. Aggregates around 8000 nm in size were observed to dominate, as indicated by the volume distribution curve (curve 1). With gradual increasing the acoustic power of ultrasonic treatment, the distribution curves of starch aggregates shifted toward decreasing the aggregate size, and the height of the volume distribution peaks also decreased. At the same time, after ultrasonic treatment, the peak of aggregate distribution in the area of 8000 nm disappeared. At acoustic power of 420 W the maximum decreasing the aggregate size to 60 nm with volume distribution of 20 % and 600 nm with volume distribution less than 10 % is observed. Thus, after exposure to ultrasound at maximum power, the size of starch aggregates decreased by more than 133 times: from 8000 nm to 60 nm.

## 2.2. Effect of ultrasonic treatment of depressor on the change in electrokinetic potential

The results of the studies of the effect of sonochemical treatment of depressors solutions on zeta-potential are shown in Fig. 4.

As can be seen from Fig. 4 (curve 1), the values of zeta potential of the CMC solution gradually shifts to the area of negative values with increasing sonochemical treatment power. In this case, the maximum negative zeta potential value of  $-35.85 \pm 1.79$  mV is observed at an ultrasonic power of 420 W. It should be noted that CMC belongs to the group of ionogenic anionic depressors, having carboxyl group in its

composition, which imparts to this agent a negative value of electrokinetic potential. As noted above (see section 2.1), ultrasound breaks the internal bonds of the CMC supramolecular structures that leads to forming expanded forms and growing anionic structures, which shift the zeta potential to the area of negative values [20, 24]. Since sonochemical treatment of CMC solution reduces zeta potential of this depressor solution, the sorption of CMC aggregates on the surface of positively charged slurry particles, such as hematite, should increase, due to which the hydrophilicity of these particles may increase.

Analysis of Fig. 4 (curve 2) shows that sonochemical treatment at any acoustic power insignificantly affects the zeta potential of starch aggregates. At the same time, the electrokinetic potential at all acoustic powers of sonochemical treatment is close to 0. The peculiarities revealed are explained by the fact that starch belongs to the group of non-ionogenic organic depressors that do not carry a charge [29, 30]. The fixation of this depressor on the surface of silicate slurry minerals, such as quartz, occurs through the formation of hydrogen bonds, where a large number of polar groups of each depressor molecule is involved, thus achieving a strong bond of the depressor with the mineral [31, 32]. It is possible that under the influence of ultrasound on the starch solution the starch aggregates, as in the case of CMC, become loose, thereby increasing the number of active polar groups, which are more firmly bound to the surface of the slurry minerals and lead to an increase in its hydrophilicity.

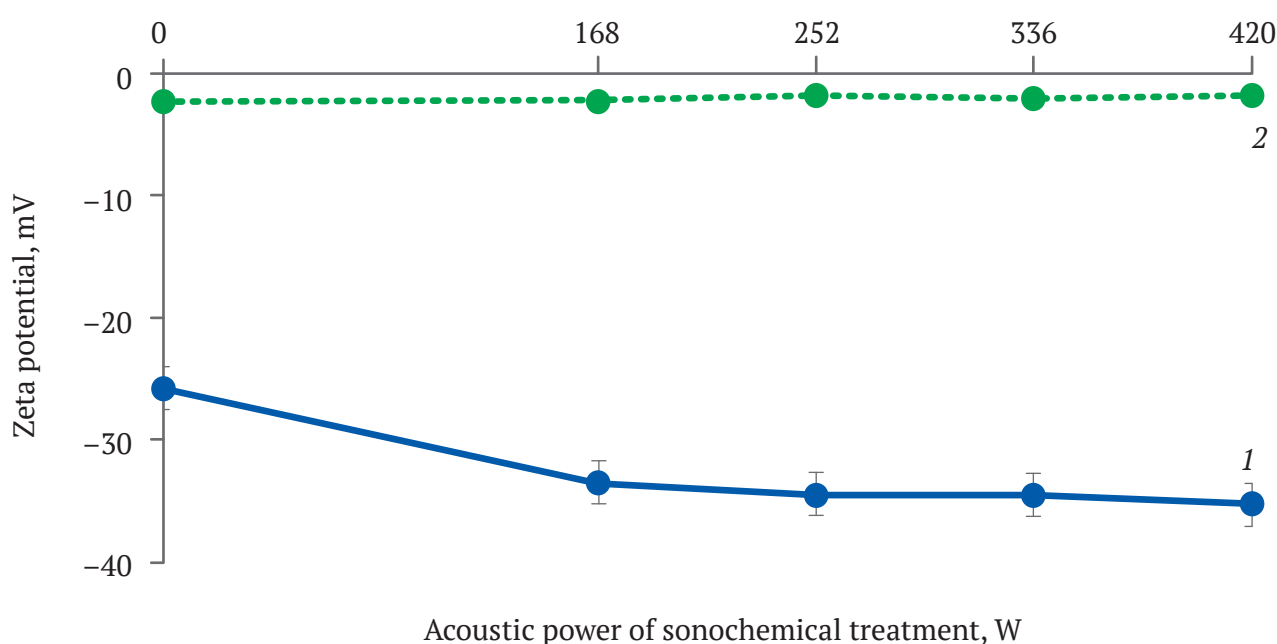


Fig. 4. Effect of ultrasonic treatment of depressor on the change in electrokinetic potential: 1 – CMC solution; 2 – starch solution



### 2.3. Influence of sonochemical treatment on viscosity-temperature properties of depressor

The effect of ultrasonic treatment of CMC and starch solutions on the change in dynamic viscosity and temperature is shown in Table 2.

The analysis of Table 2 shows that with increasing acoustic power of the agents sonochemical treatment, the dynamic viscosity of the solutions decreases, while their temperature increases. The maximum decrease in the dynamic viscosity and increase in the temperature of CMC solution are observed at sonochemical treatment acoustic power of 420 W, and these parameters reach  $5.05 \pm 0.05$  mPa-s and  $38^\circ\text{C}$ , respectively; the ultrasonic treatment of starch solution at the same acoustic power decreases the viscosity to  $2.66 \pm 0.03$  mPa-s, while the temperature of the solution increases to  $41^\circ\text{C}$ . Sonochemical treatment had the greatest effect on the starch solution, in which the dynamic viscosity decreased by 3.3 times when the maximum acoustic power of ultrasound was applied.

At the same time, as shown in Table 2, increasing the temperature of the agent solutions without using sonochemical treatment insignificantly decreased the dynamic viscosity of the solutions, indicating that the greatest contribution to the change in viscosity was made by ultrasonic treatment. It should be taken into account that sonochemical treatment generates and subsequently collapses gas bubbles

in the liquid, which locally increases pressure and temperature [21, 33, 34]. This local change in temperature raises the temperature of the entire solution and the change in pressure causes the colloidal solution aggregates to disperse, causing the viscosity of the medium to decrease.

### 2.4. Effect of sonochemical depressor treatment on the clay-salt slurry content in concentrate and KCl recovery

In the tests on flotation separation of sylvinite components, the effect of sonochemical pretreatment of depressing agents (CMC and starch) on the recovery of KCl and the content of clay-salt slurry in the concentrate was studied. In these studies, we used sylvinite ore originating from BKPRU-3 flotation plant with a high content of insoluble residue (the initial composition of the ore is presented in Table 1). The results are shown in Table 3.

It is clear from Table 3 that the application of the non-treated ultrasound CMC solution reduces the content of clay-salt slurry in the concentrate to  $22.84 \pm 0.46$  wt. % and increases the potassium chloride recovery by 1.44 % as compared to the test results where no depressor was used. Applying sonochemical treatment of CMC solution at an acoustic power of 168–252 W further increases KCl recovery and reduces the content of clay-salt slurry in the flotation concentrate (tests 3–4). At the same time the best results (increase of KCl recovery and decrease

Effect of ultrasonic treatment and increasing temperature of CMC and starch solutions on dynamic viscosity

Table 2

Depressor type	Acoustic power, W	Solution temperature, $^\circ\text{C}$	Solution dynamic viscosity, mPa-s	Solution temperature, $^\circ\text{C}$	Solution dynamic viscosity, mPa-s
	with ultrasonic treatment			without ultrasonic treatment	
CMC	0	30	$9.01 \pm 0.09$	30	$9.01 \pm 0.09$
	168	32	$7.27 \pm 0.07$	32	$8.74 \pm 0.09$
	252	35	$5.70 \pm 0.06$	35	$8.44 \pm 0.08$
	336	37	$5.18 \pm 0.05$	37	$8.24 \pm 0.08$
	420	38	$5.05 \pm 0.05$	38	$8.14 \pm 0.08$
Starch	0	30	$8.87 \pm 0.09$	30	$8.87 \pm 0.09$
	168	32	$4.18 \pm 0.04$	32	$8.27 \pm 0.08$
	252	35	$3.33 \pm 0.03$	35	$8.07 \pm 0.08$
	336	38	$2.92 \pm 0.03$	38	$7.78 \pm 0.08$
		41	$2.66 \pm 0.03$	41	$7.49 \pm 0.07$



of the slurry content) are observed at acoustic power of ultrasound of 252 W. However, further increase in the acoustic power of sonochemical treatment up to 336–420 W (tests 5–6) reduces the performance of the ultrasonic treated depressor. Similar regularities are observed when using ultrasound-treated starch (tests 8–11). The optimum acoustic power at which the maximum KCl recovery and the minimum slurry content in the flotation concentrate are observed is 252 W.

The positive effect of sonochemical pretreatment of depressors on the flotation performance is primarily due to the effect of ultrasonic cavitation, which contributes to the dispersion of large aggregates of CMC and starch (see sections 2.1 and 2.2), thereby increasing the number of active polar groups, which probably are more firmly bound with the surface of slurry particles and lead to an increase in their hy-

drophilicity, thereby improving the sylvan flotation performance.

Decreasing sylvan recovery and increasing the content of slurry in the concentrate when using high-power ultrasound-treated depressors are most likely connected with the processes of degradation and oxidation of organic macromolecules of CMC and starch, which thus lose their activity [35–37].

### 2.5. Applying sonochemical pretreatment to reduce depressor consumption

In order to confirm the possibility of reducing sylvan flotation depressor consumption, laboratory flotation tests were carried out, the results of which are provided in Table 4. Starch was chosen as the depressor since it is more efficient than KMC in increasing KCl recovery (see section 2.4). The depres-

Table 3

The effect of depressor sonochemical pretreatment on clay-salt content in flotation concentrate and KCl recovery

Test No.	Depressor	Acoustic power, W	Content of clay-salt slurry in concentrate, mass %	KCl recovery, %
1	Without depressor	Without sonochemical treatment	25.70±0.51	23.07±0.05
2	CMC	Without sonochemical treatment	22.84±0.46	24.51±0.32
3		168	21.85±0.44	25.36±1.11
4		252	9.57±0.19	29.68±2.25
5		336	11.41±0.23	28.16±0.23
6		420	17.98±0.36	25.26±1.01
7	Starch	Without sonochemical treatment	12.98±0.26	26.63±1.24
8		168	9.14±0.18	28.86±1.27
9		252	7.02±0.14	30.29±0.05
10		336	26.19±0.52	20.76±0.86
11			31.85±0.64	19.79±2.08

Table 4

Effect of ultrasound-treated depressor consumption on KCl recovery at acoustic ultrasound power of 252 W and exposure time of 150 s

Depressor consumption, g/t ore	160*	160	150	140	130	120	110	100
KCl recovery, %	55.72±0.25	62.05±2.02	60.31±0.14	59.82±0.99	59.32±1.69	57.92±3.78	54.84±0.68	52.02±0.23

\* The use of ultrasonically-untreated depressor solution.





sor consumption was reduced from 160 to 100 g/t ore in increments of 10 and only starch solution was sonochemically treated. The critical consumption of the depressor was considered to be the value after which the sylvite recovery was decreased by the next value as compared with the use of ultrasonically-untreated depressor (marked “160\*”). In these studies we used sylvite flotation feed of SKRU-3 flotation plant with low insoluble residue content, the composition of which is shown above in Table 1.

The analysis of data of Table 4 reveals that sonochemical pretreatment of the starch solution with consumption of 160 g/t ore increases the recovery of potassium chloride in comparison with the ultrasonically-untreated depressor (160\*). Decreasing the consumption of the ultrasonically treated depressor to 120 g/t ore reduces the recovery of KCl, while it remains higher by 2.2 % as compared to the KCl recovery in the test, in which the depressor was not treated with ultrasound. Further reduction of the depressor consumption to 110–100 g/t decreases the KCl recovery below the critical level (160\*) by a few percent.

Thus, the use of sonochemical depressor pretreatment not only increases KCl recovery in the sylvite flotation process, but also reduces depressor consumption. The obtained results should be tested under industrial conditions.

## Conclusion

The effect of sonochemical pretreatment of depressor reagents, CMC and starch, on dynamic viscosity, molecule aggregate size, electrokinetic potential of these agents solutions and sylvite flotation performance has been studied. It was found that the sonochemical treatment of depressor solutions decreases the size of CMC molecule aggregates from 6 to 4 nm and that of aggregates of starch molecules from 8000 to 60–600 nm. It was found that sonochemical treatment of anionic CMC solution shifts the zeta potential to the negative area with increasing acoustic power of ultrasound, but has no effect on the electrokinetic potential of nonionic starch solution. It was also found that sonochemical pretreatment of CMC and starch solutions reduces the dynamic viscosity of the agents solutions. It was revealed that sonochemical pretreatment of depressors at acoustic power of 168 and 252 W increases the recovery of KCl and reduces the content of slurry in the flotation concentrate. In addition, the possibility of reducing the consumption of the ultrasonically treated depressor was demonstrated. Thus, sonochemical pretreatment of depressors improves the sylvite flotation performance due to dispersion of the agent molecules aggregates and changes in physical and chemical properties of the depressors. This can be used in the process of flotation beneficiation of sylvite ores on commercial scale after performing pilot-plant tests.

## References

1. Huang Z., Cheng C., Zhong H. et al. Flotation of sylvite from potash ore by using the Gemini surfactant as a novel flotation collector. *Minerals Engineering*. 2019;132:22–26. <https://doi.org/10.1016/j.mineng.2018.11.055>
2. Li E., Du Z., Yuan S., Cheng F. Low temperature molecular dynamic simulation of water structure at sylvite crystal surface in saturated solution. *Minerals Engineering*. 2015;83:53–58. <https://doi.org/10.1016/j.mineng.2015.08.012>
3. Li E., Du Z., Li D., Cheng F. Specific ion effects of salt solutions on colloidal properties of octadecylamine hydrochloride. *Journal of Surfactants and Detergents*. 2017;20(2):483–491. <https://doi.org/10.1007/s11743-016-1923-7>
4. Wang X., Miller J.D., Cheng F., Cheng H. Potash flotation practice for carnallite resources in the Qinghai Province, PRC. *Minerals Engineering*. 2014;66–68:33–39. <https://doi.org/10.1016/j.mineng.2014.04.012>
5. Baturin E.N., Menshikova E.A., Blonov S.M. et al. Problems of the development of the world largest potash deposits. *Sovremennyye Problemy Nauki i Obrazovaniya*. 2012;(6):613–621. (In Russ.) URL: <https://science-education.ru/ru/article/view?id=7513>
6. Dikhtievskaya L.V., Shlomina L.F., Osipova E.O. Flotation enrichment of potash ores of different mineralogical composition. *Proceedings of the National Academy of Sciences of Belarus, Chemical Series*. 2019;55(3):277–287. (In Russ.) <https://doi.org/10.29235/1561-8331-2019-55-3-277-287>
7. Du H., Ozdemir O., Wang X. et al. Flotation chemistry of soluble salt minerals: from ion hydration to colloid adsorption. *Mining, Metallurgy & Exploration*. 2014;31(1):1–20. <https://doi.org/10.1007/BF03402344>



8. Cao Q., Du H., Miller J.D. et al. Surface chemistry features in the flotation of KCl. *Minerals Engineering*. 2010;23(5):365–373. <https://doi.org/10.1016/j.mineng.2009.11.010>
9. Chaikovskiy I.I., Korotchenkova O.V., Trapeznikov D.E. A new genetic type of leaching zone in salts of the Verkhnyaya Kama potassium salt deposit: hydrochemical, mineralogical, and structural indicators. *Lithology and Mineral Resources*. 2019;54(4):308–319. <https://doi.org/10.1134/S0024490219040023>
10. Chaikovskiy I.I. Epigenetic transformation of potassium and magnesium ores in the Verkhnyaya Kama salt deposit. In: *Rudogenez: Collection of Scientific Papers*. Miass, Ekaterinburg, 2–7 February 2008. Pp. 331–338. (In Russ.)
11. Kibanova M.S., Lanovetsky S.V. Study of the effect of slurry depressors on the performance of the rougher sylvin (potassium chloride) flotation. *Molodezhnaya Nauka v Razvitii Regionov*. 2021;1:301–303. (In Russ.)
12. Chernyshev A.V., Cherepanova M.V. Improvement of the sludge flotation stage in the processing of sylvinite. *Vestnik of Perm National Research Polytechnic University. Chemical Technology and Biotechnology*. 2020;(1):113–129. (In Russ.) URL: [http://vestnik.pstu.ru/biohim/archives/?id=&folder\\_id=9158](http://vestnik.pstu.ru/biohim/archives/?id=&folder_id=9158)
13. Vedrova V.V., Seredkina O.R., Rakhimova O.V. Methods for processing of clay-salt slurry in the production of potash fertilizers. *Molodezhnaya Nauka v Razvitii Regionov*. 2018;1:228–230. (In Russ.)
14. Ivanov A.G. Differentiation of halopelite minerals during flotation processing of sylvinite ores of the Verkhnekamskoe deposit. *Bulletin of the Perm National Research Polytechnic University. Geology, Oil and Gas and Mining*. 1999;(1):74–76. (In Russ.) URL: <https://repository.geologyscience.ru/bitstream/handle/123456789/9106/p142.pdf?sequence=1&isAllowed=y>
15. Mozheyko F.F., Potkina T.N., Shevchuk V.V., Stsefanovich S.Ch. Intensification of dehydration of clay-salt dispersion modified by macromolecular protecting reagent-depressor. *Proceedings of BSTU. No. 3. Chemistry and Technology of Inorganic Substances*. 2015;(3):35–40. (In Russ.) URL: <https://elib.belstu.by/bitstream/123456789/14999/1/mozheyko-f.-f.-potkina-t.-n.-shevchuk-v.-v.-stsefanovich-s.-ch.-intensification-of-dehydration.pdf>
16. Oliferovich D.S., Shilin L.Y., Batukov S.V., Prigara V.N. The analysis and the account of factors influencing technological process of flotation of potash ores. *Doklady Belorusskogo Gosudarstvennogo Universiteta Informatiki i Radioelektroniki*. 2009;(2):59–66. (In Russ.) URL: [https://libeldoc.bsuir.by/bitstream/123456789/31635/1/Oliferovich\\_The.PDF](https://libeldoc.bsuir.by/bitstream/123456789/31635/1/Oliferovich_The.PDF)
17. Titkov S.N., Gurkova T.M., Panteleeva N.N. et al. Potassium and potassium-magnesium ores cation flotation activation by means of new reagents. *Obogashchenie Rud*. 2005;(6):37–42. (In Russ.)
18. Kibanova M.S., Lanovetsky S.V. Review of flotation agents used in the process of sylvinite ore processing. *Molodezhnaya Nauka v Razvitii Regionov*. 2020;1:287–291 (In Russ.).
19. Xuemin Q., Hongying Y., Guobao C. et al. Inhibited mechanism of carboxymethyl cellulose as a galena depressant in chalcopryrite and galena separation flotation. *Minerals Engineering*. 2020;150:106273. <https://doi.org/10.1016/j.mineng.2020.106273>
20. Liu P., Gao W., Zhang X. et al. Effects of ultrasonication on the properties of maize starch/stearic acid/sodium carboxymethyl cellulose composite film. *Ultrasonics Sonochemistry*. 2021;72:105447. <https://doi.org/10.1016/j.ultsonch.2020.105447>
21. Iida Y., Tuziuti T., Yasui K. et al. Control of viscosity in starch and polysaccharide solutions with ultrasound after gelatinization. *Innovative Food Science & Emerging Technologies*. 2008;9(2):140–146. <https://doi.org/10.1016/j.ifset.2007.03.029>
22. Sujka M., Jamroz J. Ultrasound-treated starch: SEM and TEM imaging, and functional behaviour. *Food Hydrocolloids*. 2013;31(2):413–419. <https://doi.org/10.1016/j.foodhyd.2012.11.027>
23. Chen Y., Truong V.N.T., Bu X., Xie G. A review of effects and applications of ultrasound in mineral flotation. *Ultrasonics Sonochemistry*. 2020;60:104739. <https://doi.org/10.1016/j.ultsonch.2019.104739>



24. Poilov V.Z., Burov V.E., Gallyamov A.N., Fedotova O.A. Sonochemical activation of amine hydrochloric acid solution used as a collector in sylvinit ore flotation. *Obogashchenie Rud.* 2021;(5):15–26. (In Russ.) <https://doi.org/10.17580/or.2021.05.04>
25. Burov V.E., Gallyamov A.N., Fedotova O.A., Poilov V.Z. The ultrasonic treatment influence on pH solution of hydrochloric amine. In: *All-Russian Scientific and Practical Conference "Chemistry. Ecology. Urbanistics"*. 2021. Vol. 2. Pp. 224–227. URL: [https://ceu.pstu.ru/wp-content/uploads/2021/06/Himiyaekologiyaurbanistika\\_Tom-2.pdf](https://ceu.pstu.ru/wp-content/uploads/2021/06/Himiyaekologiyaurbanistika_Tom-2.pdf)
26. Liu H., Du Y.M., Kennedy J.F. Hydration energy of the 1,4-bonds of chitosan and their breakdown by ultrasonic treatment. *Carbohydrate Polymers*. 2007;68(3):598–600. <https://doi.org/10.1016/j.carbpol.2006.11.004>
27. Liu P., Wang R., Kang X. et al. Effects of ultrasonic treatment on amylose-lipid complex formation and properties of sweet potato starch-based films. *Ultrasonics Sonochemistry*. 2018;44:215–222. <https://doi.org/10.1016/j.ultsonch.2018.02.029>
28. Savitri E., Juliastuti S.R., Handaratri A. et al. Degradation of chitosan by sonication in very-low-concentration acetic acid. *Polymer Degradation and Stability*. 2014;110:344–352. <https://doi.org/10.1016/j.polymdegradstab.2014.09.010>
29. Wu Z., Qiao D., Zhao S. et al. Nonthermal physical modification of starch: An overview of recent research into structure and property alterations. *International Journal of Biological Macromolecules*. 2022;203:153–175. <https://doi.org/10.1016/j.ijbiomac.2022.01.103>
30. Huang J., Wang Z., Fan L., Ma S. A review of wheat starch analyses: Methods, techniques, structure and function. *International Journal of Biological Macromolecules*. 2022;203:130–142. <https://doi.org/10.1016/j.ijbiomac.2022.01.149>
31. Titkov S.N. Activation of the action of cationic collecting reagents. *Journal of Mining Institute*. 2005;165:191–195. (In Russ.) URL: <https://pmi.spmi.ru/index.php/pmi/article/view/8289>
32. Bocharov V.A., Khachatryan L.S., Ignatkina V.A., Baatarhuu J. On the selection of copper-molybdenum sulfide concentrate division methods with the use of high molecular weight organic depressors. *Mining Informational and Analytical Bulletin*. 2007;(8):235–242. (In Russ.)
33. Shen H., Guo Y., Zhao J. et al. The multi-scale structure and physicochemical properties of mung bean starch modified by ultrasound combined with plasma treatment. *International Journal of Biological Macromolecules*. 2021;191:821–831. <https://doi.org/10.1016/j.ijbiomac.2021.09.157>
34. Osipovich A.E., Vakhrushev V.V., Kazantsev A.L. et al. Ultrasonic treatment influence on aqueous emulsion of amine hydrochloride. *Vestnik of Perm National Research Polytechnic University. Chemical Technology and Biotechnology*. 2014;(3):89–96. (In Russ.) URL: [https://vestnik.pstu.ru/biohim/archives/?id=&folder\\_id=4235](https://vestnik.pstu.ru/biohim/archives/?id=&folder_id=4235)
35. Xu M., Xing Y., Gui X., Cao Y., Wang D., Wang L. Effect of ultrasonic pretreatment on oxidized coal flotation. *Energy Fuels*. 2017;31(12):14367–73. <https://doi.org/10.1021/acs.energyfuels.7b02115>
36. Deb Barma S., Sathish R., Baskey P.K., Biswal S.K. Chemical beneficiation of high-ash indian noncoking coal by alkali leaching under low-frequency ultrasonication. *Energy Fuels*. 2018;32(2):1309–1319. <https://doi.org/10.1021/acs.energyfuels.7b03291>
37. Barma S.D. Ultrasonic-assisted coal beneficiation: a review. *Ultrasonics Sonochemistry*. 2019;50:15–35. <https://doi.org/10.1016/j.ultsonch.2018.08.016>

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