Al-Farabi Kazakh national university

Sulfur nanoparticles: production, research, application

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Almaty, September 13, 2018

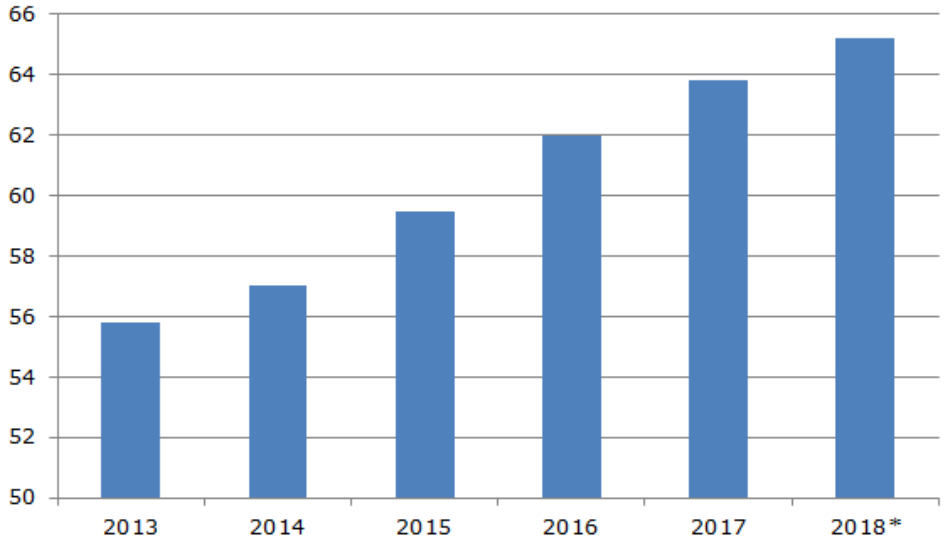
Sulfur production

Kazakhstan produces about 3 M tons of sulfur annually, including over 1 M tons from Kashagan.

A drop in demand for sulfur is observed.

Overproduction of sulfur is a challenge!

World production of sulfur



https://marketpublishers.ru/lists/11561/news.html

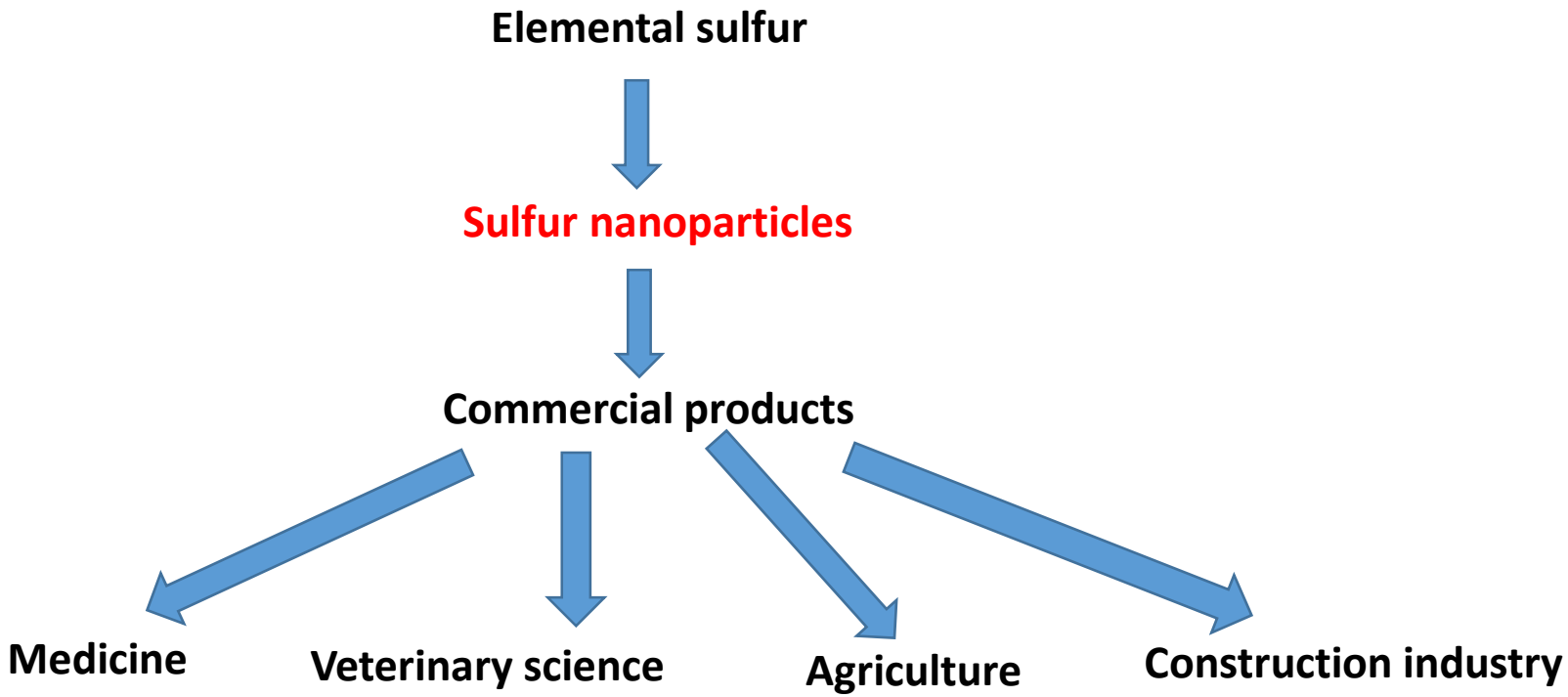
Development of new ways of processing elemental sulfur

Obtaining new knowledge-based commercial products containing sulfur nanoparticles is an attractive idea.

Solution of this task involves the conduct of scientific research.

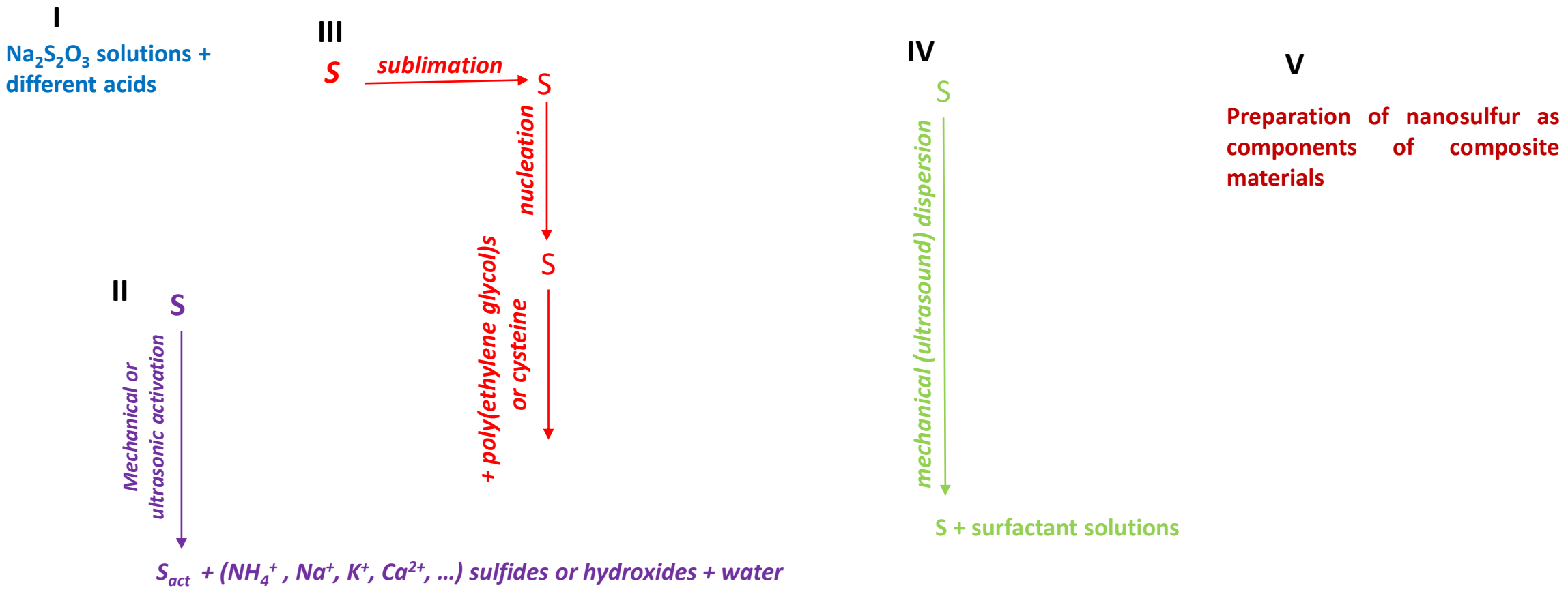
This work was carried out in al-Farabi KazNU under the program *«Development of new methods for obtaining sulfur nanoparticles for the development of technologies for the producing preparations of various functional purposes» (2015-2017).*

Research objective

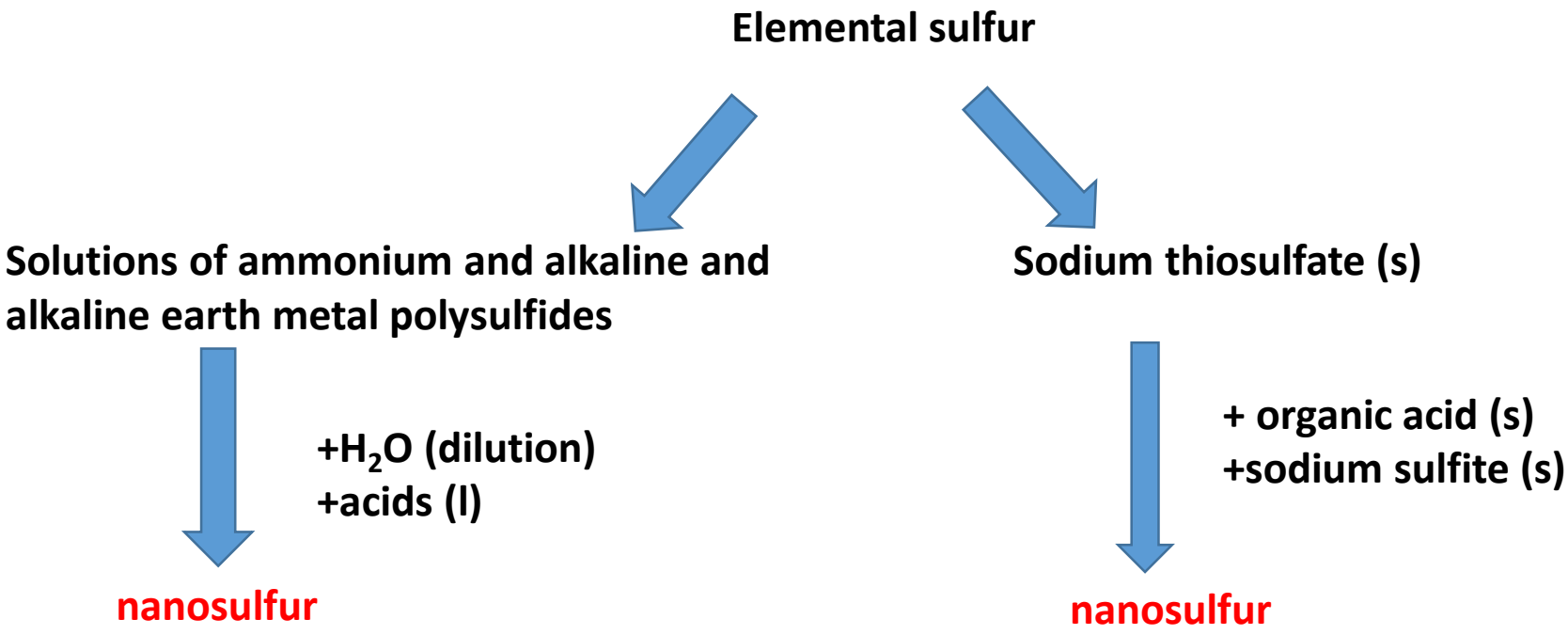


How to obtain sulfur nanoparticles?

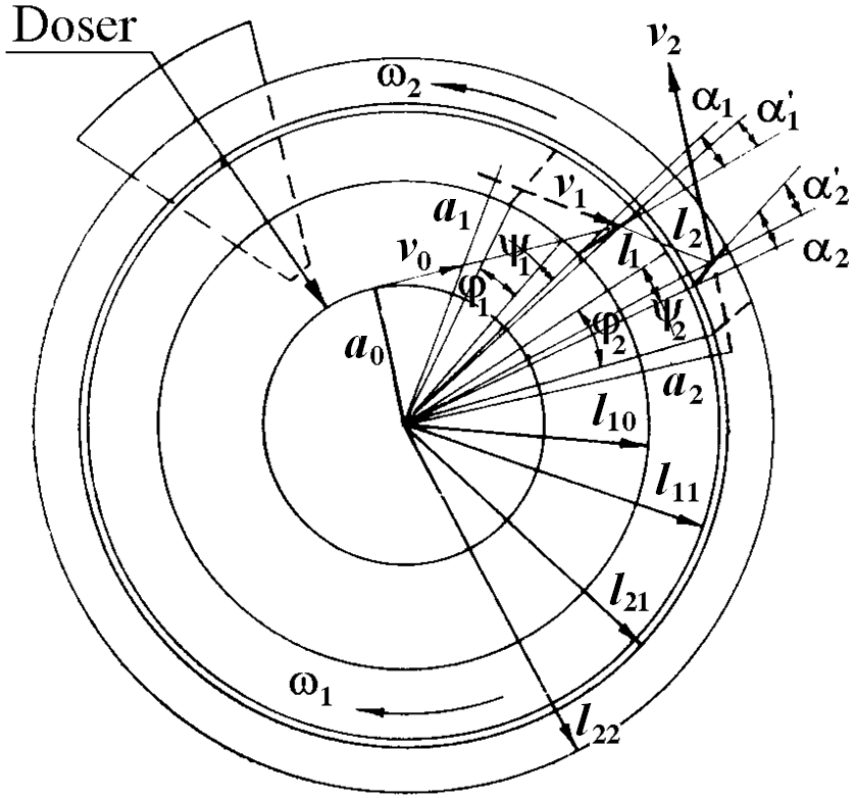
Available methods for producing nanodispersed sulfur (5 approaches are known):



Nanosulfur obtaining within this work



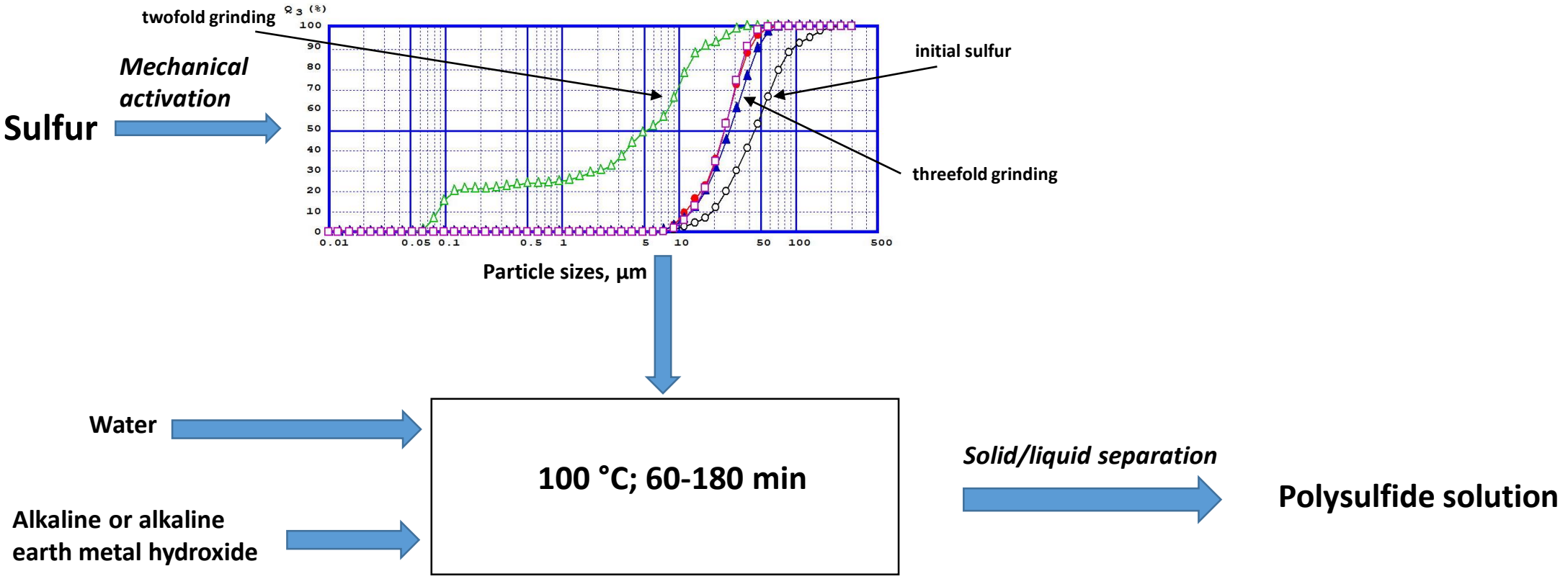
Modeling sulfur milling process in disintegrator



- ***kinematic and dynamic*** characteristics of elastic and inelastic collisions of particles of processed rhombic sulfur with rows of disintegrator fingers are calculated;
- ***advices on selecting*** optimal conditions for activation milling of α-sulfur in the disintegrator are given;
- ***the results*** can be partially used in the processing of sulfur and in other types of shock grinding devices, in particular, jet mills.

Urakaev, F. H., Massalimov, I. A., Yusupov, T. S., Uralbekov, B., Tatykaev, B. B., Galiyeva, P. A., ... & Burkitbayev, M. M. (2016). Моделирование активационного измельчения частиц ромбической серы в дезинтеграторе. Chemical Bulletin of Kazakh National University, (3-4), 10-20.

Polysulfide solutions obtaining



Calcium polysulfide solution obtaining in semi-industrial scale

- **Chemical reactor (6 m^3)**
- **4 tons of product per one loading cycle (d=1.25 g/cm^3)**

The work was carried out jointly with the Bashkir State University (Ufa, Russia)

Conversion of calcium polysulfide

Calcium polysulfide

Strong (100 times or more) dilution with water

Hydrosol of sulfur

Storage at low temperatures (about 0 ∘ C)

Evaporation

Polycrystals of calcium polysulfide

Monocrystals of calcium polysulfide

Nanosulfur obtaining from polisulfide solutions

+H_2O (dilution)

$Na_2S_4 + H_2O \rightarrow NaOH + NaHS_4$

$NaHS_4 \rightarrow NaOH + H_2S_4$

$H_2S_4 \rightarrow H_2S\uparrow + S\downarrow$

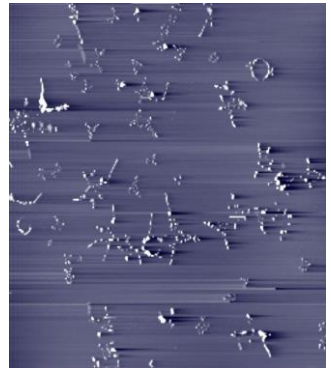
+ acids

$CaS_4 + 2HNO_3 \rightarrow H_2S\uparrow + \mathbf{3S}\downarrow + Ca(NO_3)_2$

$3H_2S + 2HNO_3 \rightarrow \mathbf{3S}\downarrow + 2NO^- + 4H_2O$

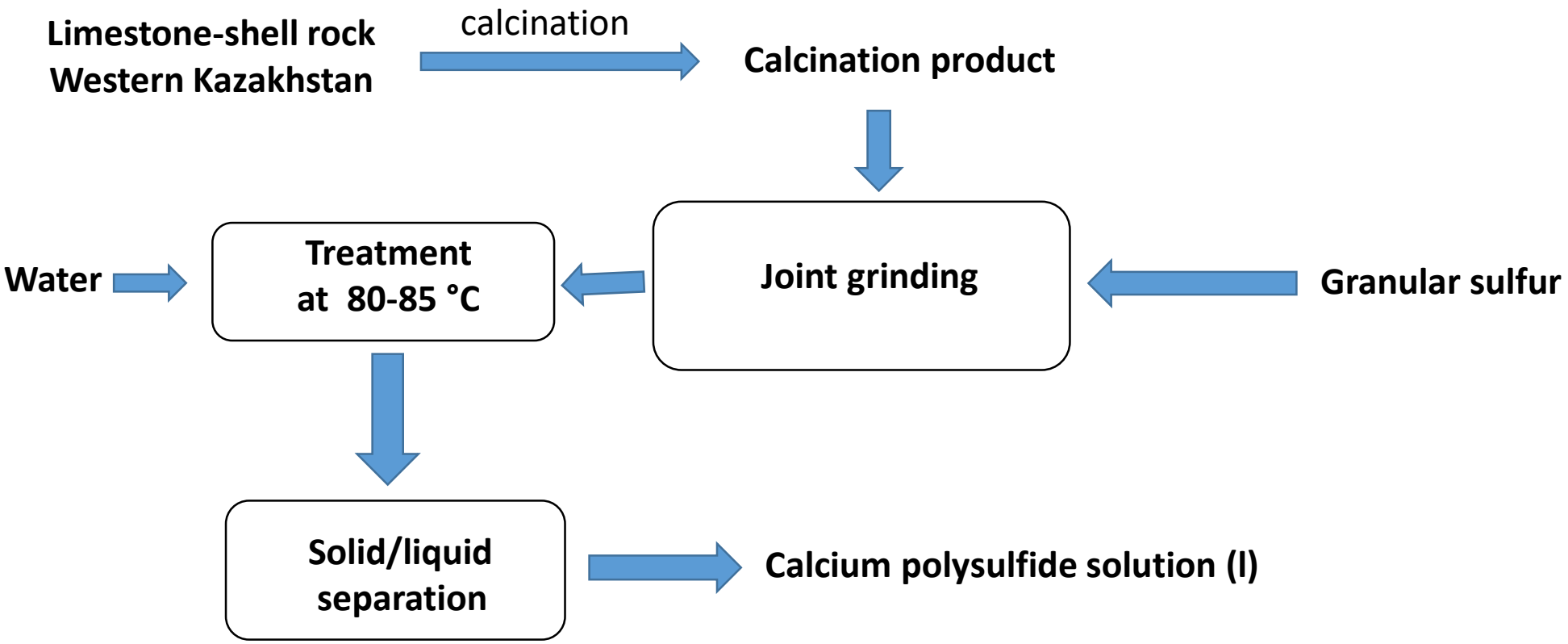
$H_2S - 2e^- = \mathbf{S} + 2H^+$

$NO^-_3 + 4H^+ + 3e^- = NO + 2H_2O$



SEM image of sulfur particle (20 nm)

Energy-saving way of obtaining calcium polysulfide solution



RK Patent application No.2017/1211.1

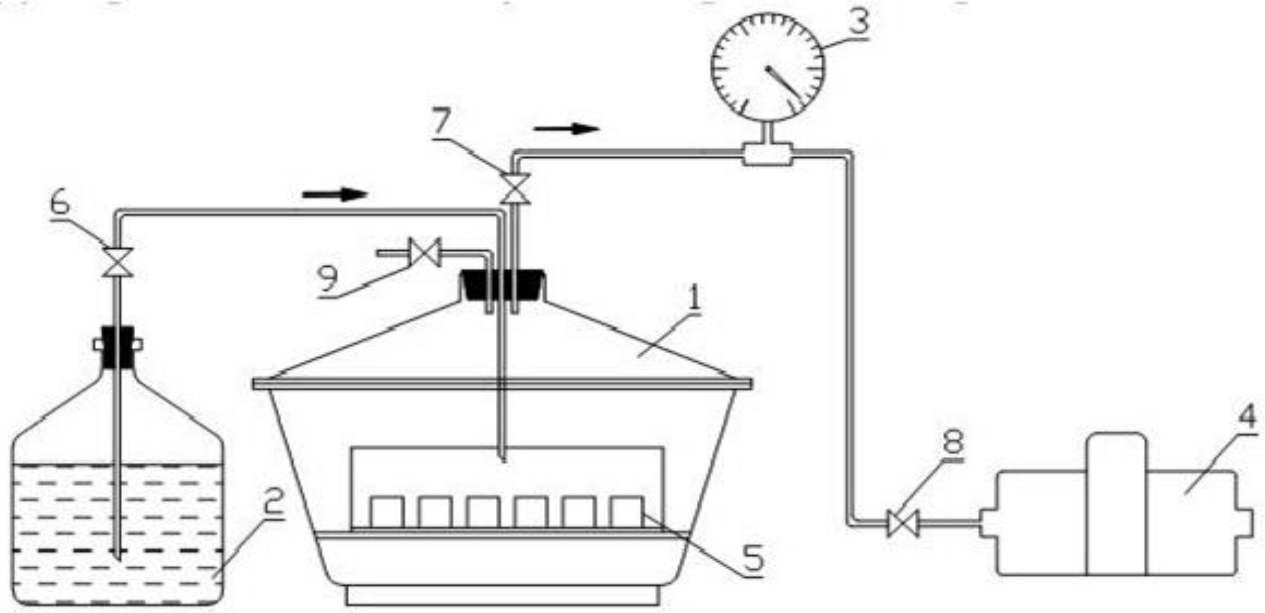
Development of impregnating compounds for building materials hydrophobization

Polysulfide solution → **Impregnation** ← **Concrete samples**

↓

Testing of processed samples

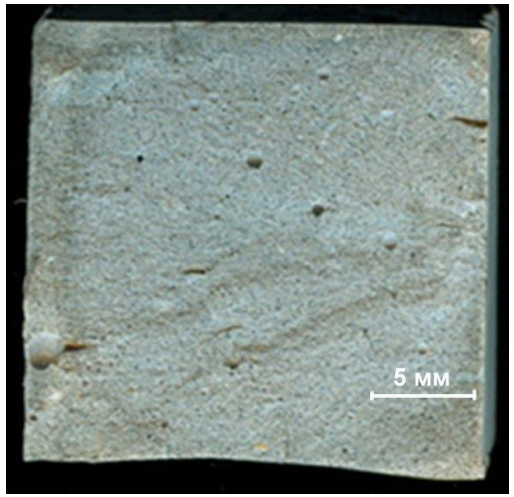
Development of impregnating compounds for hydrophobization of building materials



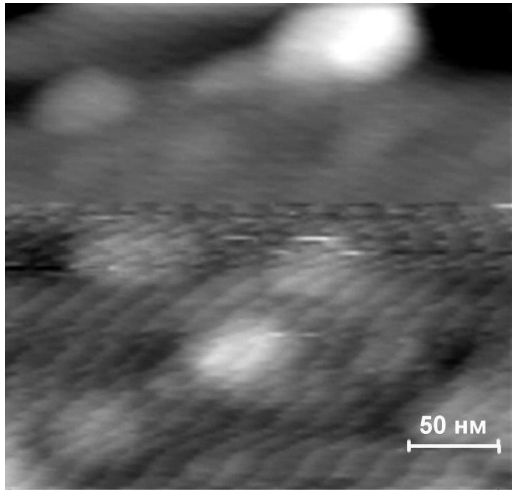
1 - vacuum desiccator; 2 – container with impregnating solution; 3 - vacuum gauge; 4 - vacuum pump; 5 - impregnating bath with samples; 6-9 – taps.

Preliminary evacuation and subsequent impregnation of samples

Development of impregnating compounds for hydrophobization of building materials



(a)



(b)

Image (a) and SEM image (b) of concrete impregnated with calcium polysulfide

Impregnation leads to the appearance of hydrophobic particles in the pores of concrete sample.

Treated concrete sample becomes practically waterproof in conditions of frontal action of water.

Development of a sulfur-containing solution to accelerate plant growth

Field tests demonstrated that the nanosulfur, isolated from sulfur-containing solution , has a growth-stimulating effect on wheat, peas, grapes and tomato.

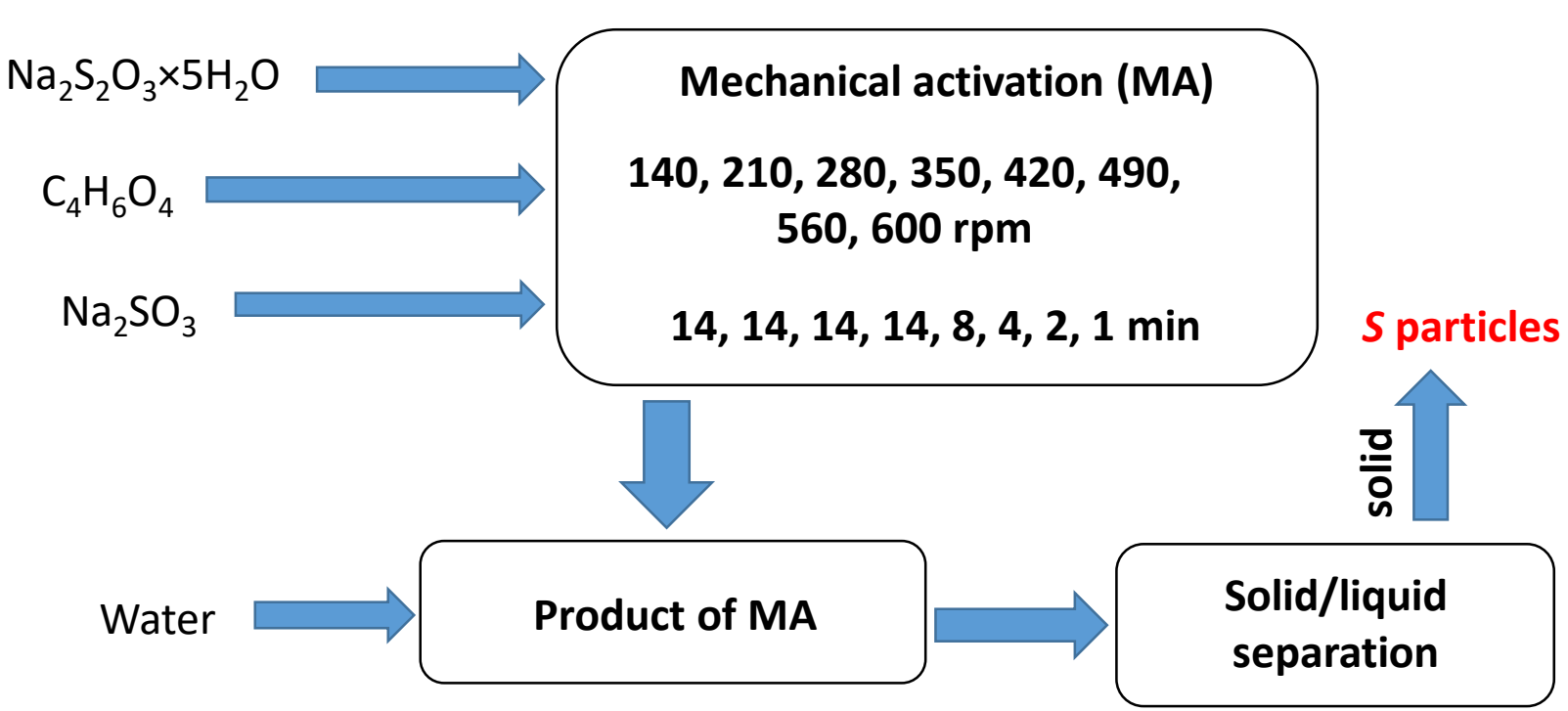
•For wheat, a maximum (28%) increase in protein content in the grain is achieved.

•For peas, the yield increase reaches 40-45%.

•For grapes, the level of infection decreases from 34% to 1%.

• For tomato, complete destruction of harmful fungi occurs.

Mechanochemical synthesis of colloidal sulfur particles in $Na_2S_2O_3$-$H_2(C_4H_4O_4)$ -$Na_2S_2O_3$ system



Pulverisette **planetary-type ball mill**

Urakaev, F. K., Bulavchenko, A. I., Uralbekov, B. M., Massalimov, I. A., Tatykayev, B. B., Bolatov, A. K., ... & Burkitbayev, M. M. (2016). Mechanochemical synthesis of colloidal sulfur particles in the Na2S2O3–H2(C4H4O4)–Na2SO3 system. Colloid Journal, 78(2), 210-219.

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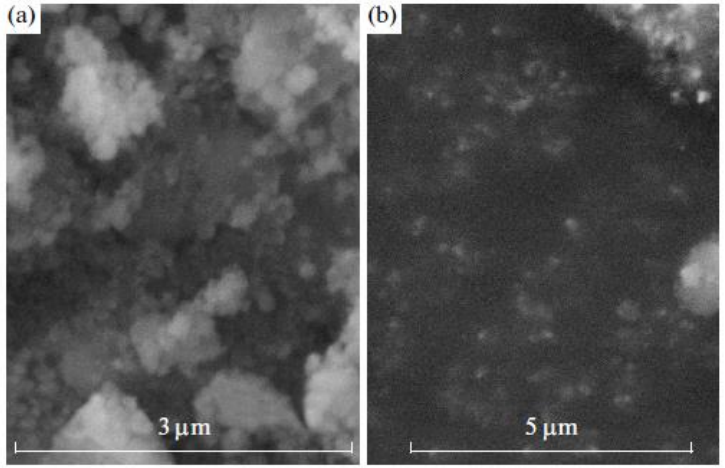
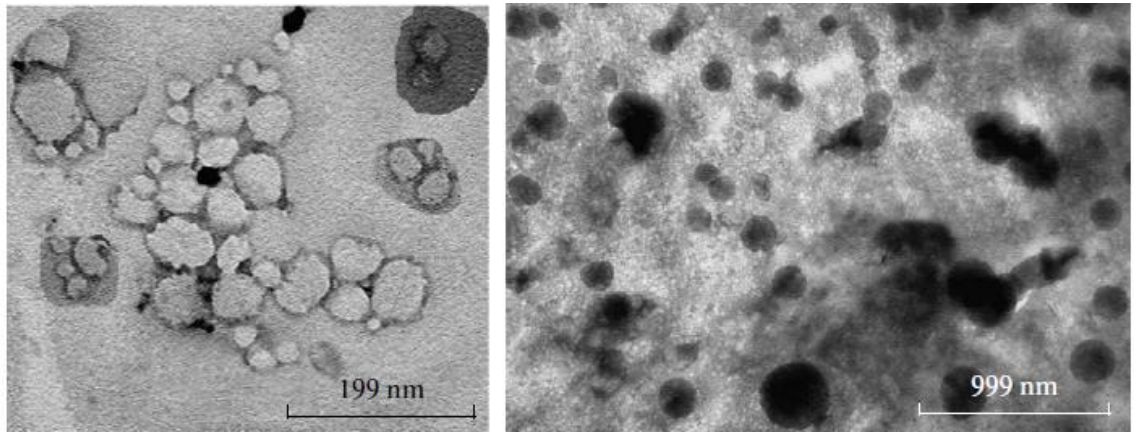


SEM images of (a) mechanically activated sample and (b) sulfur particles washed out of the sample



TEM images of (a) mechanically activated sample assembles from different regions of visual field at 100 000 × magnification and sulfur particles washed out (200 000 ×) (b)

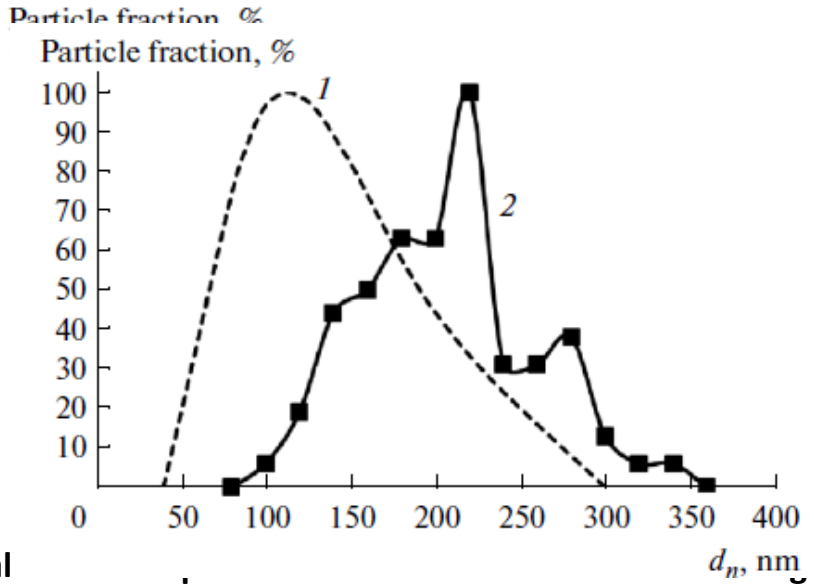
Urakaev, F. K., Bulavchenko, A. I., Uralbekov, B. M., Massalimov, I. A., Tatykayev, B. B., Bolatov, A. K., ... & Burkitbayev, M. M. (2016). Mechanochemical synthesis of colloidal sulfur particles in the Na2S2O3–H2(C4H4O4)–Na2SO3 system. Colloid Journal, 78(2), 210-219.

Mechanochemical synthesis of colloidal sulfur particles in $Na_2S_2O_3$-$H_2(C_4H_4O_4)$ -$Na_2S_2O_3$ system

$$Na_2S_2O_3 \cdot 5H_2O + yC_4H_6O_4 + zNa_2SO_3$$
$$= (z+1)Na_2SO_3 + yC_4H_6O_4 + 5H_2O + S_n^0.$$

$Na_2S_2O_3$ is a source of sulfur
Na_2SO_3 and **$C_4H_6O_4$** play the roles of catalyst and diluent

z=19.6



Normal dynamic light scattering (a) and TEM (b)

Urakaev, F. K., Bulavchenko, A. I., Uralbekov, B. M., Massalimov, I. A., Tatykayev, B. B., Bolatov, A. K., ... & Burkitbayev, M. M. (2016). Mechanochemical synthesis of colloidal sulfur particles in the Na2S2O3–H2(C4H4O4)–Na2SO3 system. Colloid Journal, 78(2), 210-219.

Mechanochemical synthesis of anhydrous sodium thiosulfate

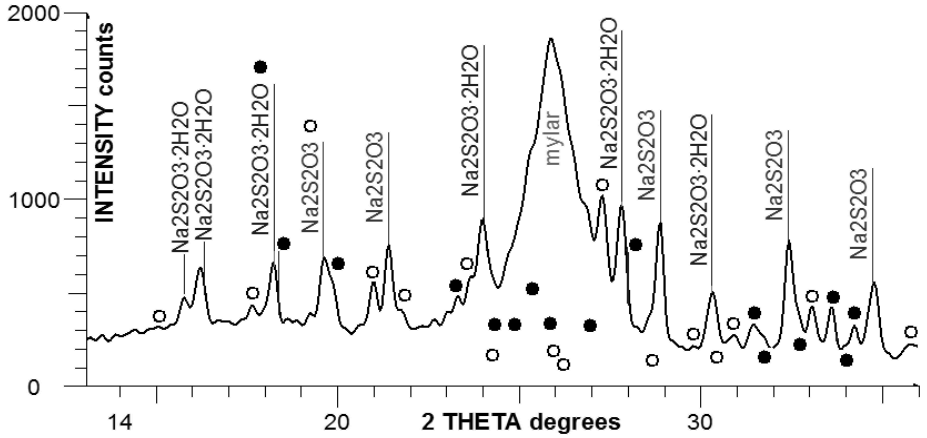
$$S + Na_2SO_3 \rightarrow Na_2S_2O_3$$

Sulfur

Sodium sulphite

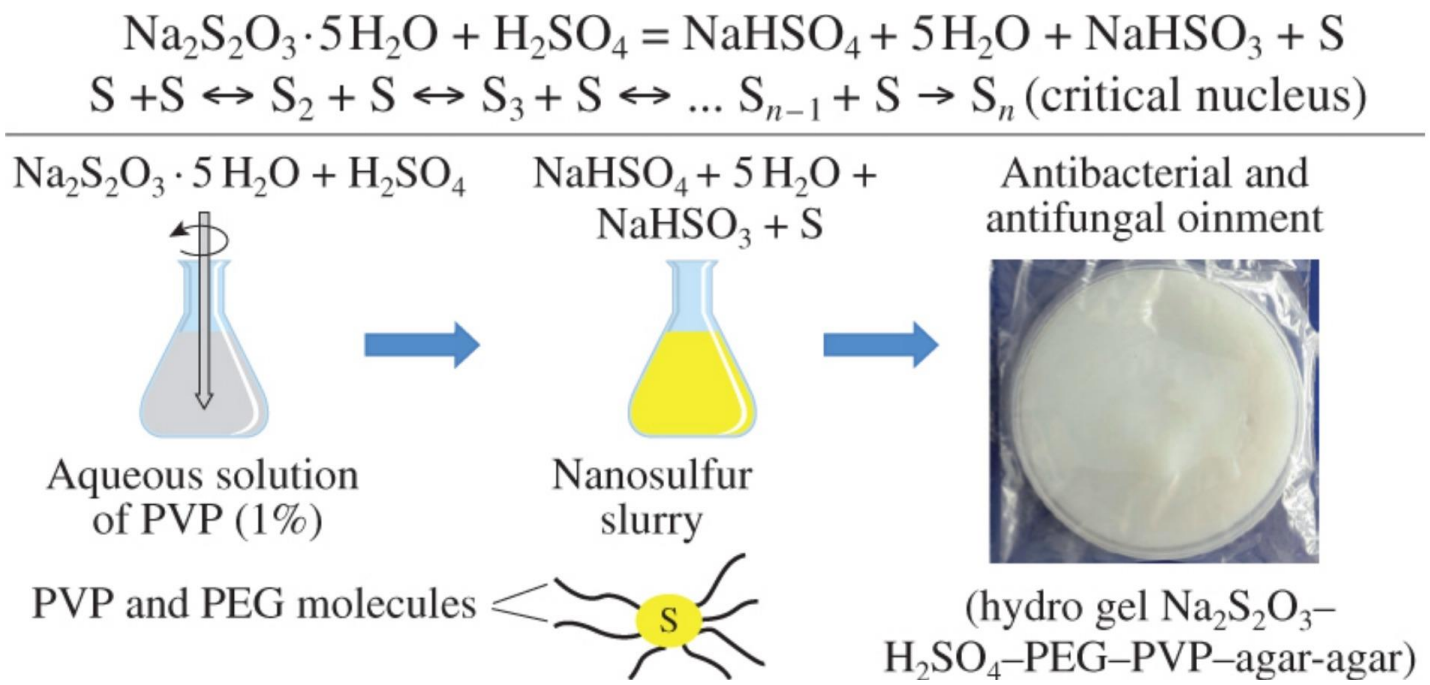
Mechanical activation in planetary ball mill

Sodium thiosulfate (yield 93-95%)



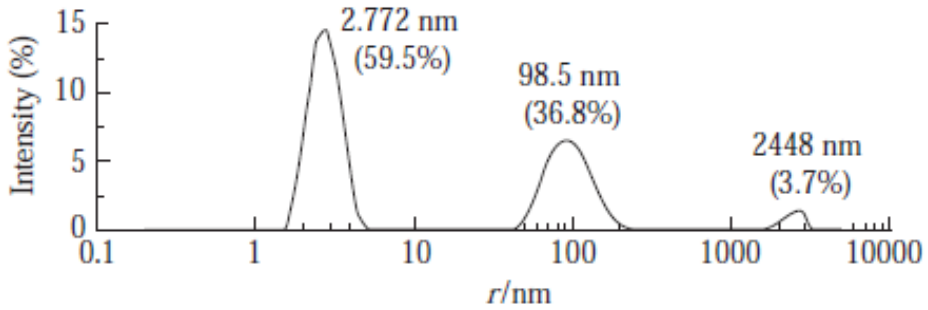
Patent of RK, No. 32560, publ. 12/20/2017

Sulfur nanoparticles stabilized in the presence of water-soluble polymers

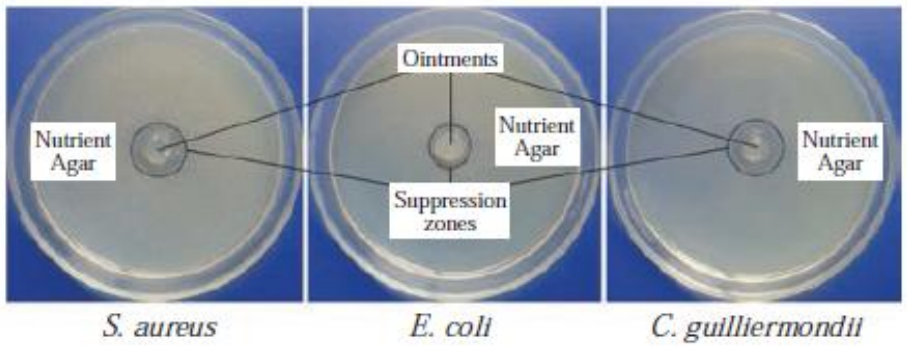


Graphical abstract from ***Urakaev, F. K., Abuyeva, B. B., Vorobyeva, N. A., Mun, G. A., Uralbekov, B. M., & Burkitbayev, M. M. (2018). Sulfur nanoparticles stabilized in the presence of water-soluble polymers. Mendeleev Communications, 28(2), 161-163.***

Sulfur nanoparticles stabilized in the presence of water-soluble polymers



Typical size distribution of sulfur



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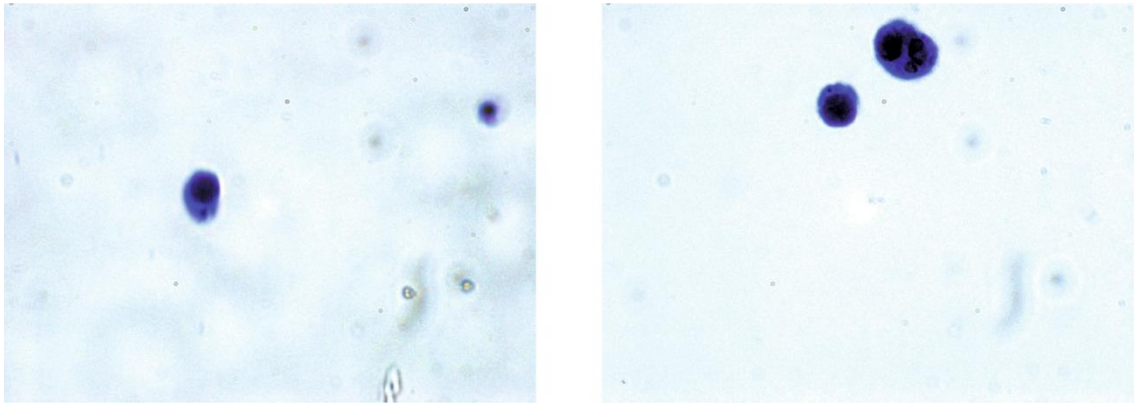
Mutagenic activity of sulfur nanoparticles

- **Cytotoxicity and genotoxicity** of sulfur nanoparticles (SNPs) of about 70 nm in size were examined on the L5178Y mouse lymphoma cell culture. The concentration of SNPs causing 50% cell death is 0.078–0.312 mg/mL.
- **Micronucleus assay** revealed no mutagenic properties of SNPs. Metabolic activation of SNPs by the rat liver microsomal fraction does not affect the toxicity.
- **Mechanism of cytotoxic** action is associated with the interaction of elemental sulfur with sulfhydryl groups of molecules inside the cell.



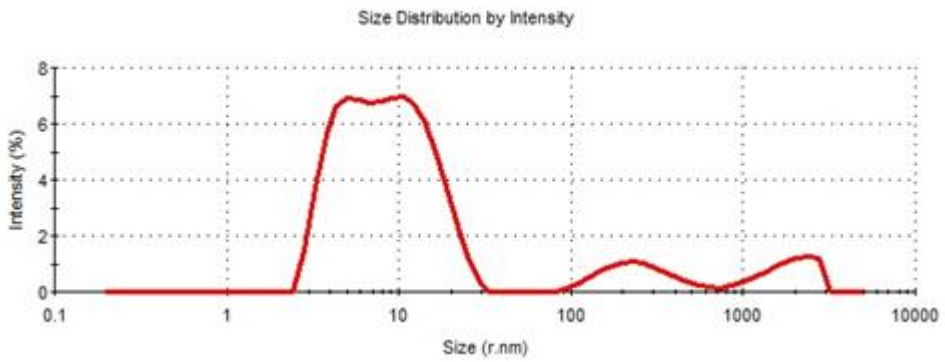
(a) **(b)**

Micronuclei (arrows) in L5178Y cells (positive control) cultured with MMC (a) and CP (b)

Islamov, R. A., Bishimova, I., Sabitov, A. N., Ilin, A. I., & Burkitbaev, M. M. (2018). Lack of Mutagenic Activity of Sulfur Nanoparticles in Micronucleus Test on L5178Y Cell Culture. Cell and Tissue Biology, 12(1), 27-32.

Preparation of polymeric composite dressings with nanosulfur for use in medicine

$Na_2S_2O_3$ + polyvinylpyrrolidone + polyethylene glycol + agar-agar + H_2O



Size of sulfur nanoparticles in a solution of polyvinylpyrrolidone

Polymeric hydrogel dressing with nanosulfur

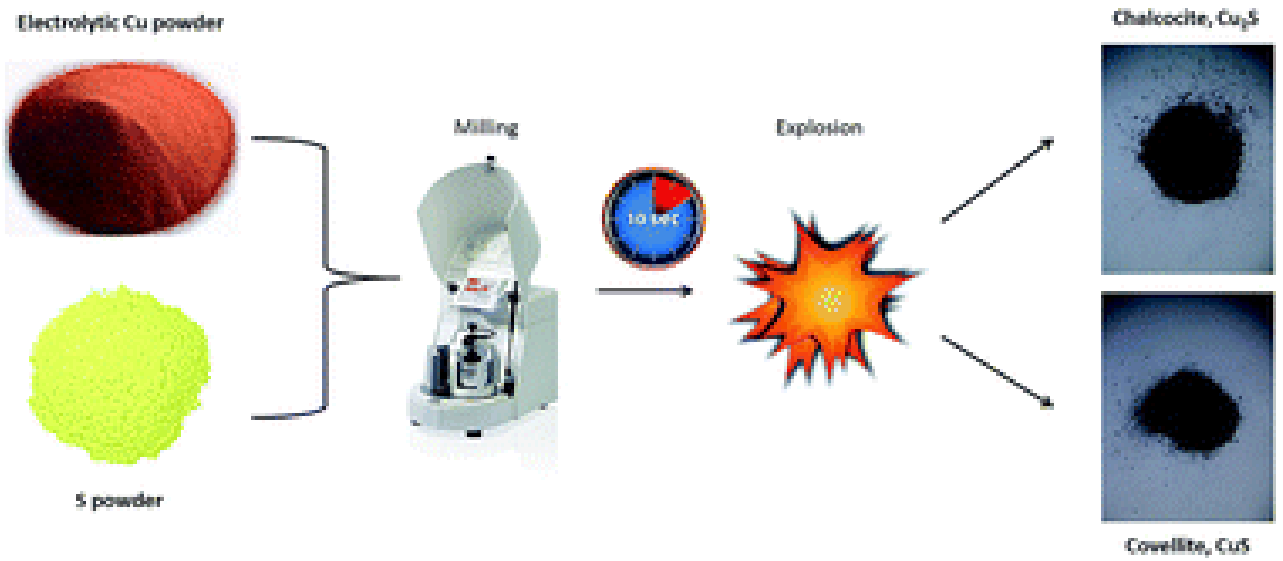
Dressings exhibit antifungal and antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli* and *Candida guilliermondii*.

Ultrafast mechanochemical synthesis of copper sulfides

•Covellite, CuS and chalcocite, Cu_2S were prepared within a few seconds by ball milling of the elemental precursors.

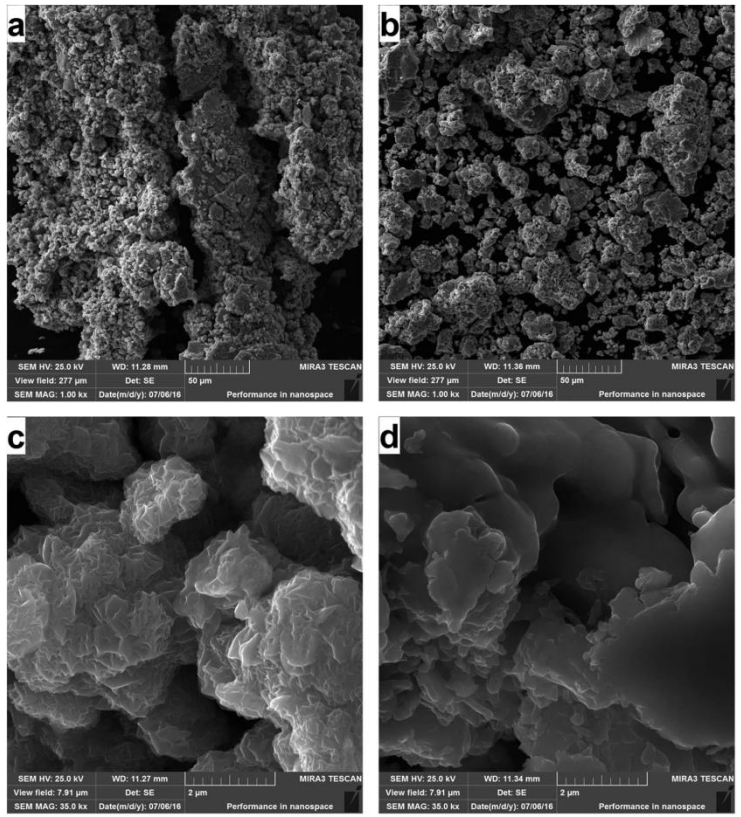
•The local temperature at the contact site between the milling media and the milled mixture at the time of explosion was calculated as 950 °C for CuS and 700 °C for Cu_2S.

•The mean crystallite size of the prepared products was 15 nm for CuS and 65 nm for Cu_2S.

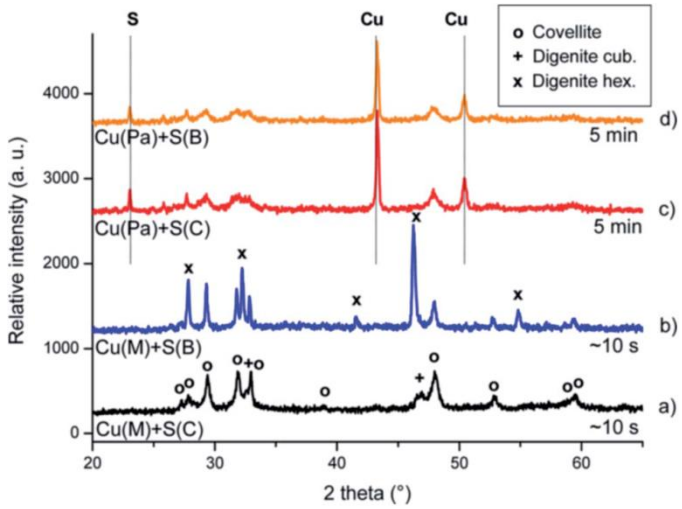


Baláž, M., Zorkovská, A., Urakaev, F., Baláž, P., Briančin, J., Bujňáková, Z., ... & Gock, E. (2016). Ultrafast mechanochemical synthesis of copper sulfides. RSC Advances, 6(91), 87836-87842.

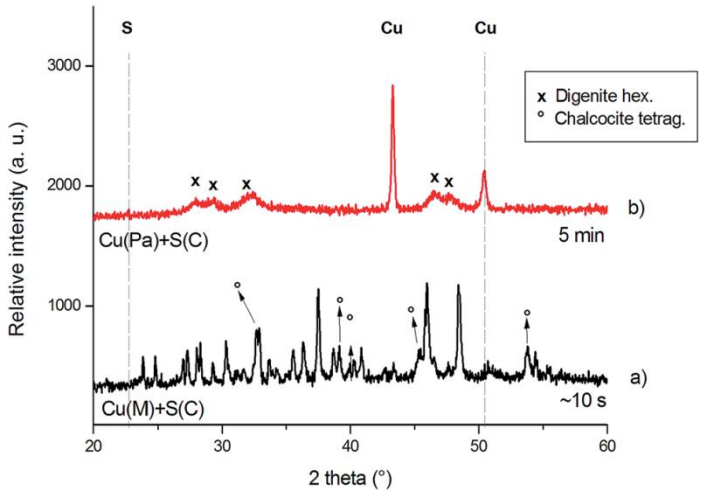
Ultrafast mechanochemical synthesis of copper sulfides



SEM micrographs of the prepared products: CuS (a) and Cu2S (b); highly magnified micrographs for CuS (c) and Cu2S (d).



Cu : S 1 : 1 mixtures



Cu : S 2 : 1 mixtures

XRD patterns of the milled mixtures

Baláž, M., Zorkovská, A., Urakaev, F., Baláž, P., Briančin, J., Bujňáková, Z., ... & Gock, E. (2016). Ultrafast mechanochemical synthesis of copper sulfides. RSC Advances, 6(91), 87836-87842.

Collaborators

- Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences (Novosibirsk, Russia)
- Bashkir State University (Ufa, Russia)
- Institute of Geotechnics of the Slovak Academy of Sciences (Koshice, Slovakia)
- Scientific Center for Anti-Infective Drugs JSC (Almaty, Kazakhstan)

Conclusions

- **mechanochemical methods** for the production of polysulfide solutions and sodium thiosulfate have been developed;
- **methods of obtaining** sulfur nanoparticles from polysulfide solutions, as well as from sodium thiosulfate, have been proposed;
- **energy-saving technology** for the production of a sulfur-containing solution for use in agriculture (growth-stimulating preparation) as well as in the construction industry (hydrophobizer) has been created;
- **mechanochemical method** for obtaining colloidal sulfur particles in the system $Na_2S_2O_3$-H_2 ($C_4H_4O_4$) -$Na_2S_2O_3$ has been proposed;

Conclusions

- **mechanochemical route** for the fast production of copper sulfide from copper and elemental sulfur has been developed;
- **possibility of stabilizing** sulfur nanoparticles in the presence of water-soluble polymers has been demonstrated;
- **polymeric composite** dressings containing nanosulfur, for use in medicine, have been created;
- **mutagenic activity** of sulfur nanoparticles has been investigated.

Thank you for attention