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Effect of cavitational conditioning of water on stability of coal-water slurry

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Abstract. Coal-water slurry (CWS) is the basis of modern alternative fuel - coal-water fuel (CWF). To produce stable coal-water slurry, i.e. coagulation and separation is an important technological problem. The paper studies CWS the disperse part of which is fine brown Kansk-Achinsk coal, the dispersive part is distilled water. Effect of cavitational conditioning on CWS stability has been studied. The efficiency was for the first time studied by magnetic resonance tomography (MRT). In the experiment spin-lattice relaxation time profiles T1 were recorded along the central vertical axis of the samples. T1 dynamics correlates well with the local density of CWS solid phase. MRT data was sequentially interpreted with rheological characteristics of CWS. Feasibility of applying MRT method to find out time and space evolution of CWS has been estimated. The MRT methods has been shown to be efficient in resolution of technological problems to improve consumer properties of the coal-water fuel.

1. Introduction

In accord with the Energy strategy of Russia the coal energy should develop along the road of modernizing and implementing new clean coal technologies [1]. Among these technologies is the coal-water fuel (CWF). This alternative fuel is a slurry the dispersed phase of which is coal, including fine low-grade coal with mass content from 45 to 70 % by wt, and the dispersal medium is water of different quality, process water including. The coal-water fuel can be produced from anthracites, bituminous, brown coals of different grades and ash content, water of any quality, mine and industrial water including. Among the most important characteristics of the fuel from the standpoint of its storage, transportation and combustion is its dynamic stability. Successful use in practice of highly concentrated systems comprising solid phase necessitates comprehensive investigation of their properties; kinetic and aggregative stability, i.e. steady concentration homogeneity of disperse phase particles in the volume of dispersion medium hold a special place.

Among methods of improving CWF qualities are the impact on the entire coal-water system or preliminary treatment of disperse or dispersion parts. The water molecules exhibit express polarity determining branched hydrogen bonding distributed over the water volume and can be grouped. The

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areas with elevated content of hydrogen bonding are generally thought to be clusters. Specifics of structural configuration of water and its metastability allow it to respond to external impact of any nature [2-4]. Under targeted exposure to external physical fields (electrical, magnetic, electromagnetic, thermal, radiation, mechanical, acoustic, etc.) the water changes its properties. In many cases to activate chemical processes, to implement new ways of synthesis and accelerate reactions in the system it is expedient to expose water to cavitation [5-7]. The authors of [8] describe CWF preparation scheme employing preliminary activation of water (water conditioning) in cavitation rotary-pulse apparatus (RPA). This made possible to evade the problem of fast wear of the equipment employing cavitators to process and homogenize directly CWF. The work studied highly concentrated CWS based on Kansk-Achinsk brown coal and distilled water prepared by the methods of cavitation water conditioning in hydrodynamic rotary generator.

2. Materials & Methods

2.1. Methods of measurement

Size distribution of the CWS solid phase was estimated by dry fractionation on screens and with CPS DiscCentrifuge DC 2400. Dynamic viscosity of CWS was measured with rotational viscosimeter Rheotest-2. pH was measured with HannaInstruments WaterTest instrument. Electronic images were produced with transmission electron microscope JEOL-JEM-200CX, optical images – with OLUMPUS BX43 microscope (Japan, ×100). Sedimentation properties were studied by two methods:

1. Measurement of coal particle sedimentation velocity. Relative sedimentation volume was measured $V = V_{sediment} \setminus V_v$, where $V_{sediment}$ is the volume of sediment formed at time moment t; V_v is the volume of the slurry.

2. Method of magnetic resonance tomography (MRT). The measurements were carried out with NMR microtomograph on the basis of Bruker AVANCE DPX 200 (radio-frequency coil diameter – 25 mm), software PARAVISION 4.0.

Sedimentation properties have been studied by measuring particle sedimentation velocity and H^1 NMR microtomography. Electron magnetic resonance was used to study the electron structure of dispersed phase of CWS. EMR spectrometer of X-range SE/X-2544 (Bruker) was used.

2.2. Preparation of samples

Cavitation-activated water $H_2O(2)$ was made in rotary hydrodynamic generator with two-blade wedge-shaped impeller (wedge angle 60°), motor power 1 kW, effective volume of chamber 10^{-4} m^3 for 5 min at rotational speed of the rotor 10000 rpm in supercavitation mode. For this the distilled water GOST 6709-72 was processed at 20 ^{0}C – H_2O (1). CWS was prepared by crushing the coal in laboratory mill MBL-100 and wet grinding in Waring 8010D instrument-based laboratory blender. Turbulent microstirring in preparation of CWS made possible to produce homogeneous mixtures of water and coal in the form of nontransparent viscous paste with fine coal particles content (≤ 50 μm) in the slurry ≈60%:

CWS1: coal powder (75 g) and distilled water (75 ml) were stirred in blender Waring 8010D for 3 min at rotational speed of the rotor 10000 rpm, bimodal distribution of particles by size – 50…3.5 μm;

CWS2: coal powder (75 g) and cavitation-activated distilled water (75 ml) were stirred in blender Waring 8010D for 3 min at rotational speed of the rotor 10000 rpm, bimodal distribution of particles by size – 50…3.8 μm;

CWS3: coal powder (75 g) and distilled water with addition of 0.1 n of NaOH solution (75 ml) were stirred in blender Waring 8010D for 3 min at rotational speed of the rotor 10000 rpm.

For MRT investigation CWS was poured into an ampoule with inner diameter 22 mm and placed into the NMR microtomograph sensor. Initial level of all samples – 40mm, studies were carried out at 20 ^{0}C.

The samples under study are represented in the table.

Table. Physical-chemical parameters of the samples.

Sample	Time between preparation and measurement, min	pH	T ^{0}C
CWS1	0	5.71	34.2
CWS1	30	5.75	24.2
CWS2	0	5.69	36.7
CWS2	30	5.76	26.4
$H_2O(1)$	0	4.79	20.0
$H_2O(2)$	0	6.20	30.0

3. Experimental results. Discussion

3.1. Rheological properties of CWS

Investigation of dynamic viscosity of CWS (figure 1a, b), prepared on distilled water (pH = 4.79) with preliminary cavitation conditioning of the water (activated water pH = 6.2) showed that in both cases CWS can be considered pseudoplastic fluid in which dependence of the shear stress on the shear rate obeys the power law. Dynamic viscosity of CWS2 (line 2 in figure 1), prepared on activated water is on the average 30% less than the viscosity of CWS1 (line 1 in figure 1) in the shear rate range.

Transition from pseudoplastic flow to plastic for CWS2 is less than for CWS1 (figure 1b).

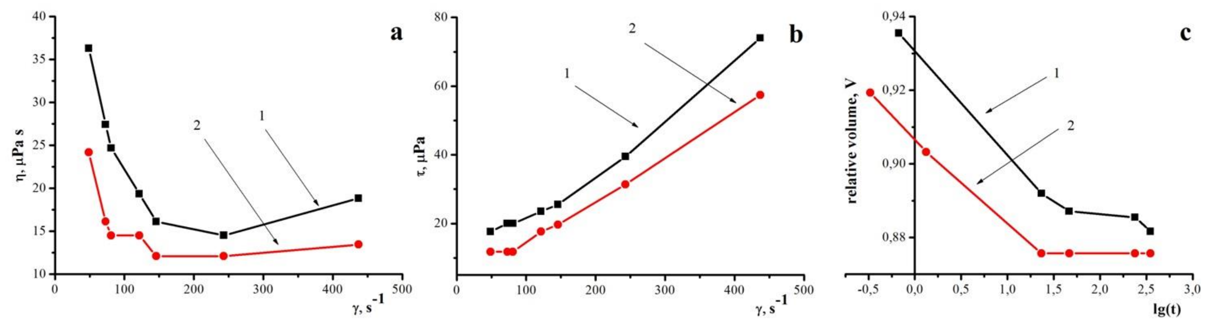

Figure 1. Rheological curves 1 – CWS1, 2 – CWS2: (a) dynamic viscosity η depending on the shear rate at 25 ^{0}C, (b) complete rheological curves of the flow, (c) variation curves of relative sedimentation volume V with time t in coordinates (lg(t), V).

The sedimentation curve for CWS2 is below the curve for CWS1 (figure 1c), i.e. the coagulation capacity of disperse phase of CWS2 is below than that of CWS1 (volume of sediment is less).

3.2. Investigation of CWS by MRT

NMR microtomograph visualized proton-containing dispersal medium of CWS. The spin system (water proton system) is in the external magnetic field (4.7 T), and is excited by inhomogeneous field in the form of pulses, the image is formed by response of the spin system to this excitation [9, 10]. Because of the presence of solid coal particles, the image is inhomogeneous and contains information about the state of water-coal colloidal system. Figure 2 shows the phases of sediment (dark part) and of suspension with variable composition (light part).

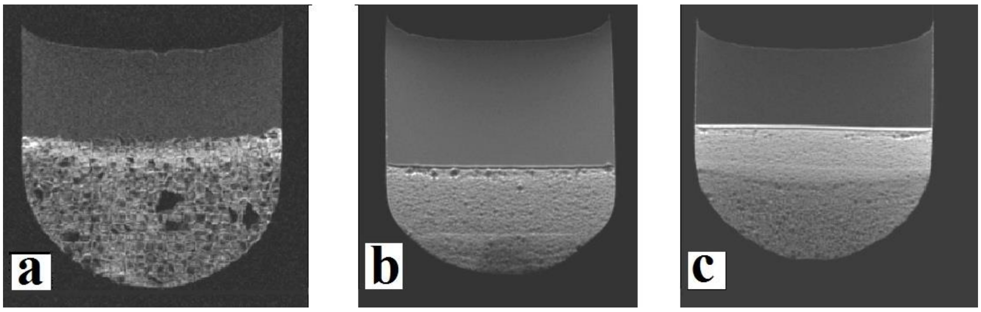

Figure 2. NMR-tomographic image of spin density of nuclei H[1] in the «coal-water» system: (a) CWS «coal-water» initial simple stirring, (b) CWS1, (c) CWS2.

Profiles of spin-lattice relaxation intensity times T1 along the vertical axis of the sample were built for the qualitative characteristics of H[1] NMR images (figure 3). T1 value depends on the physical-chemical characteristics of the investigated object, correlates with local density of the solid phase.

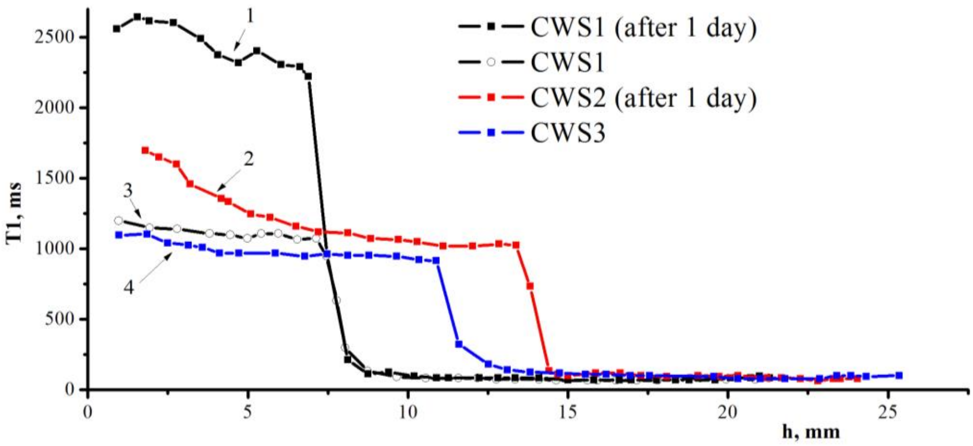

Figure 3. Vertical profiles of time T1 of CWS samples with different dispersion media: 1 – CWS1 (one day after preparation), 2 – CWS2 (one day after preparation), 3 –CWS1, 4 – CWS3.

Factors determining quantitative value of T1 are physical-chemical characteristics of the investigated object (molecular structure, temperature, viscosity, chemical composition, etc.). From figure 3 it is apparent that the sedimentation properties of CWS1 and CWS2 differ. One day after preparation almost all solid fraction in CWS1 precipitated, precipitation is observed in CWS2, too, but in smaller amount.

Coal-water slurries are known to exhibit the tendency of improving rheological properties in the alkaline medium. This effect is clearly seen on T1 curves (figure 3). The sediment in CWS3 is smaller than in CWS1. So, the NMR images of CWS make possible to trace dynamics of condition of the coals-water slurry depending on most diverse conditions of both dispersion and disperse media. It also makes possible to solve such technological problems as dependence of rheological characteristics of CWS on the properties of the liquid phase, on the oxidation level of coal surface, on the composition of mineral impurities, etc.

3.3. CWS coagulation structures
The process of preparing CWS is based on mechanochemical activation which destroys the structure of coal. The coal decomposes into organic and mineral components. CWS forms chemically active dispersion medium saturated with components from mineral constituents of coal of ionic and cationic

form with pH different for water $H_2O(1)$ and $H_2O(2)$. The surface of forming coal particles features elevated reactive capacity, because of adsorption hydrophilic centers form which actively interact with the water molecules.

Present in the cavitation-activated water are H^+ and OH^- ions, H* and OH* radicals, products of decomposition of hydrogen peroxide H_2O_2, active water molecules [11]. All of them can be additional sources of hydrophilic centers. Owing to H-bonds clusters of water molecules and continuous monomolecular H_2O films form around hydrophilic centers. As a result, the amount of bound water in CWS2 increases. The observed «shear thinning» of CWS2 is determined by the feasibility of water molecules to form branching H-bonds and participate in different interactions of van der Waals type between the disperse and dispersion media; this results in destruction of the mesh structure of CWS. When the disperse phase reaches certain concentration spatial bulk structure forms. Such a structure emerges due to formation of coagulation contacts between the particles through liquid medium interlayer. The condition necessary for the coagulation structure to emerge is the presence in the solid phase of particles of colloidal size capable of Brownian motion. Distributing over the slurry volume together with large particles they form a special three-dimensional wireframe consisting of chains or aggregates (figure 4d) [12]. The increasing amount of bound water in CWS2 promotes increase of coagulation structures and, consequently, improves rheological properties of CWS, plasticizes and elasticizes it. This fact was noted in synthesis of CWS2.

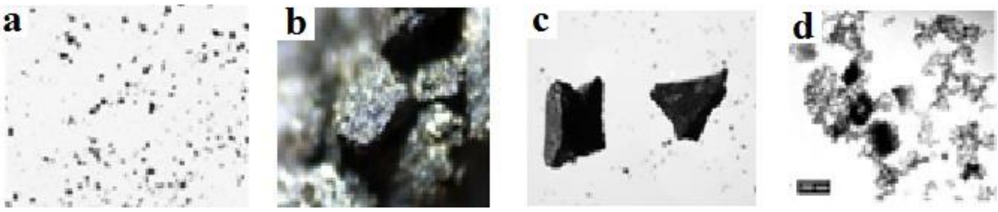

Figure 4. Coal particles in CWS: (a) coal powder, (в) surface of coal particle, (c) shape of coal particles, (d) EM image of CWS coagulation structures.

According to the EPR data destruction of the coal structure initiates changes in the electron structure of the coal particles surface. Emergence of coagulation structures comprising enlarged particles of iron oxides and other elements is noted by emergence of additional superthin lines in the EPR spectra [13].

4. Conclusions

1. Efficiency of targeted control of physical-chemical properties of high-viscosity slurries – cavitation conditioning of water for CWS dispersion medium – has been studied.

2. The cavitation conditioning of water in hydrodynamic rotary generator in synthesis of brown-coal-based coal-water slurry is shown to decrease dynamic viscosity of CWS on the average by 30% and over the entire range of shear rates.

3. The cavitation conditioning of water improves sedimentation characteristics of CWS.

4. Utilizing MRT method the authors visualized spatial distribution of proton density of the dispersion medium in the process of sedimentation of fine coal particles in nontransparent coal-water slurry.

5. The paper is the first to demonstrate potential of magnetic resonance tomography (MRT) to study physical-chemical properties of nontransparent coal-water slurries to solve a broad range of technological problems associated with improvement of consumer characteristics of the coal-water fuel.

6. In CWS the cavitation-activated water acts as a stabilizing addition. Depending on the type of used cavitators, processing modes, coal type the efficiency of its impact on CWS properties will differ. It seems expedient to consider activation of the dispersion phase as an additional method of improving CWS technological parameters along with chemical additions.

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