

# UNDERSTANDING THE EFFECT OF STRUCTURAL DEFECTS IN GRAPHITE ON THE PROPERTIES OF FOUNDRY COATINGS

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## ABSTRACT

How the properties of protective coatings form is a complex mechanism that is yet to be studied. Because of the lack of such understanding, researchers predominantly rely on an empirical method to create protective coatings that would offer a necessary performance. In quality terms, the process of building a protective layer involves two stages: Stage 1 — properties formed during preparation in liquid state; Stage 2 — structure formed while the coating is drying. Properties start to form even during preparation when liquid protective coatings experience such processes as ion adsorption, electrocapillary and electrokinetic phenomena, material and energy transport through colloid systems, electrostatic interaction between colloidal particles. These processes govern the overall future performance and efficiency of protective coatings. The electrical double layer and the potentials arising in it play a major role in these processes. This research aims to understand the properties of aqueous suspensions with natural and mechanically activated graphites. The graphite was activated in an AGO-2 planetary centrifugal mill. The findings show that the sedimentation stability of suspensions and coatings is governed by the size of the electrical double layer in graphite particles. Due to mechanical activation, the electrical double layer of graphite grows from 0.3 to 0.4 mV, while the sedimentation stability after 24 h of settling rises from 66 to 76% and from 87 to 97% with the concentrations of graphite being 30 and 50 w/w per 100 w/w of water, correspondingly. Accumulation of structural defects in graphite particles contributes to the growth of the electrical double layer at the surface of graphite particles. This makes the contact area of the interacting phases — i.e. graphite and water — larger and produces active nuclei on the freshly produced surface.

## Introduction

The physical and mechanical properties and processing behaviour of molding and core sands, as well as protective coatings, are governed by the structure, properties and number of their components [1, 2].

How the properties of protective coatings form is a complex mechanism that is yet to be studied. Because of the lack of such understanding, researchers predominantly rely on an empirical method to create protective coatings that would offer a necessary performance [3–10 et al.].

Having analyzed the literature [1–11 et al.], we established that, in quality terms, the process of building a protective layer involves two stages (**Table 1**): Stage 1 — properties formed during preparation in liquid state; Stage 2 — structure formed while the coating is drying.

Properties start to form even during preparation when liquid protective coatings experience such processes as ion adsorption, electrocapillary and electrokinetic phenomena, material and energy transport through colloid systems, electrostatic interaction between colloidal particles. These processes govern the over-

all future performance and efficiency of protective coatings. The electrical double layer and the potentials arising in it [2, 12–14] play a major role in these processes.

In dispersion systems, the electrical double layer, which is a layer of ions that forms on the surface of a particle (at the particle–dispersion medium interface) as a result of ion adsorption from the solution or dissociation of surface compounds. The electrical double layer creates an electrical potential, the values of which at different points are relevant to the surface potential, adsorption layer potential, zeta-potential [15].

The electrokinetic potential is determined by the surface characteristics of interfacing phases. Graphite surface is inert, i.e. it does not have ionizable groups and can

Table 1. Coating formation stages

Stage	Processing factors	Properties	Physical & chemical factors defining how the components interact
Liquid state	Filler quality Composition Mixing technique Preparation regimes (mixing intensity & time)	Density Viscosity Sedimentation stability	Wettability, electrical double layer, interfacial tension, adsorption, absorption, etc.
Solid state	Composition Application: with a brush/sprayer Mould: composition, surface roughness, porosity, temperature Drying process: temperature, time	Modified strength Thickness of the coating and penetrating layer Gas permeability	Paint filtration through mould pores, cohesion and adhesion, etc.

Activation time, min.	Filler concentration, per 100 w/w of water	Viscosity acc. to VZ-4, s	Sedimentation stability, %, after			
			5 min	30 min	1 h	3 h
0	30	11	88	69	66	66
	40	12	98	86	83	81
	50	13	98	90	87	87
	60	15	100	97	93	90
	70	Paste				
10	30	15	97	86	84	74
	40	18	100	97	94	86
	50	21	100	97	97	96
	60	Paste				
20	30	18	98	86	87	76
	40	21	100	98	95	86
	50	24	100	99	99	97
	60	Paste				
30	30	17	100	91	87	81
	40	18	100	100	98	93
	50	Paste				

only become electrically charged as a result of specific ion adsorption [16].

The quality of the graphite surface can be modified as required by applying different activation techniques [17–22]. Among them, mechanical activation [17, 18, 23–26] would be the most advanced one.

This research aims to understand the properties of aqueous suspensions with natural and mechanically activated graphites.

### Experimental Methods

Natural cryptocrystalline graphite of the Kureyka deposit [18] was chosen for the experimental study.

The graphite was activated in an AGO-2 planetary centrifugal mill. The activation regimes are discussed in the papers [18, 27, 28].

The electrical double layer of the aqueous suspensions was analyzed with a Dispersion DT-310 electroacoustic spectrometer described in the paper [29].

Methods for determining sedimentation stability are specified in GOST 10772–78. Settled suspensions were analyzed after 5 and 30 minutes and also after 1, 3, 7 and 24 hours after the start of the test.

### Results

**Table 2** shows the results of the tests conducted for graphite suspensions with natural and activated graphite. The concentration of graphite varied from 30 to 60%, the activation time — from 10 to 30 minutes.

The above data clearly indicate that the sedimentation stability of all the suspensions in view tends to decrease as the settling time extends (up to 24 h).

Diluted suspensions (with low concentrations of the filler) are freely dispersed (or, structureless) systems.

As the filler concentration goes up, it activates forces that create a particular structure, i.e. a spatial grid, and the suspension becomes a paste. For natural graphite, this state transition occurs when the concentration of graphite is 60 w/w per 100 w/w of water.

As the activation time gets longer, the sedimentation stability and viscosity of the suspensions tend to rise, since during activation the graphite particles become more dispersed and active and capable of attracting more of the liquid phase molecules. As a result, the particles lose the ability to move freely in the liquid phase, cohesion forces arise (the repulsive forces are able to counteract the adhesive forces), and the particles become kinetically interdependent.

This, in turn, speeds up the structure building process leading to a quicker into-paste transition. Thus, when using

mechanically activated graphite for 20 min. a suspension turns into a paste with the filler concentration being above 50 w/w of graphite; when mechanically activated graphite is applied for 30 min., such transition happens with the filler concentration being above 40 w/w of graphite.

By looking at the data given in Table 1, one can conclude that the results obtained confirmed the outcomes described in the papers [18, 27, 28]: 20 minutes would be the optimum graphite activation time.

The following explanation can be given to support the obtained results: In the course of mechanical activation the graphite structure sees both stacking faults and bonding defects [30–33].

The stacking faults imply missequenced parallel layers of perfect hexagonal grids in the carbon atoms. They occur due to weak interlayer bonding when the graphite layers can shift easily causing missequencing [34]. This explains why the crystal system is changing during mechanical activation: P6/mmc → P3 after 20 and 30 min. of cryptocrystalline graphite activation [28].

The grid bonding defects include vacancies and their groups of impurity atoms embedded in the hexagonal layer; isometric bonding defects (when a portion of atoms have sp hybridization), edge defects, etc. [30–33]. These defects can be viewed as damages caused by different factors, and they cannot just be attributed to “broken” interatomic bonds. In fact, “broken bonds” can characterize various defects — from vacancies to macroscopic cracking [23].

During mechanical activation, the intermolecular bonds break following a particle integrity failure, which can be described with a two-stage model. The first stage sees a delocalized accumulation of bonding defects in a particle, whereas the second stage is characterized with a localized growth of the fracture nucle-

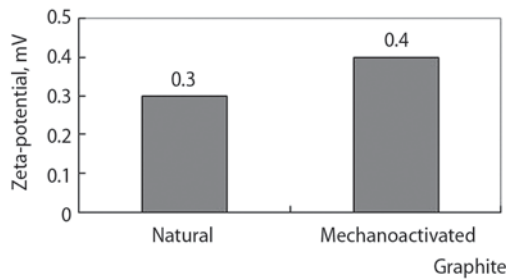


Fig. 1. Zeta-potential of the Kureyka deposit graphite

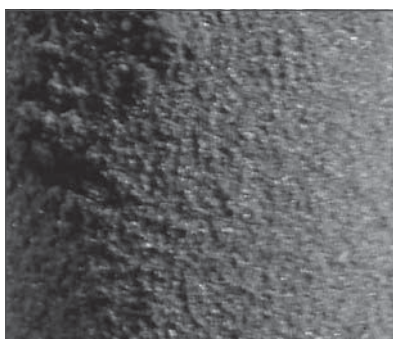
Component	Concentration, % wt.
Burnt sand	70–80
Quartz sand	4–7
Bentonitic clay	5–6
Water	5–7
Liquid glass	6–10

us resulting in a main crack that destroys the graphite particle [35].

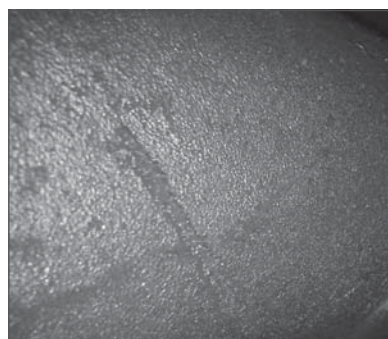
The unbalanced bonds and free radicals that emerge as a result of failure have “extra” energy, and they initiate further physical and chemical reactions, including the reactions between graphite and water that occur in the suspension. Such interaction leads to a growth of the electrical double layer in the interfacial area in the “activated graphite - water” system (Fig. 1). The graphite was activated in an AGO-2 planetary centrifugal mill for 20 minutes.

Due to the increased value of the electrical double layer, the aqueous suspensions with activated graphite tend to be more stable, which is beneficial for the performance of foundry coatings in liquid state.

The designed coatings were tested at the “Enisey” repair and maintenance facility in Krasnoyarsk, where 89 castings in the weight range of 3.5 to 90 kg were produced from the SCh20 and SCh25 cast iron grades. The pouring temperature was 1,400 °C. The mould and/or core were coated for casting. The mixture composition is given in Table 3.



a



b



c

Fig. 2. Surface quality:

a — no coating; b, c — coatings made with graphites of various quality: b — GLS-2(K); c — GLS-2A(K)

Basic coating	Burnt-on thickness, $\mu\text{m}$
No coating	4503–5465
Natural graphite	3370–3500
Mechanically activated graphite	900–1000

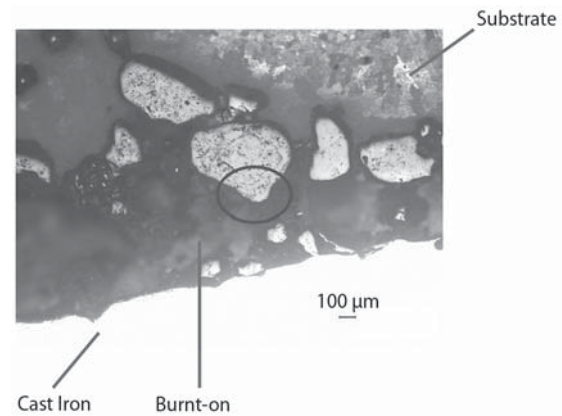


Fig. 3. Burnt-on in a casting

Surface quality of the castings is shown in Fig. 2.

The trial showed that the castings that were produced normally — i.e. without protecting coatings, have burnt-ons (Fig. 3) on the surface, which consist of heat-affected sand grains impregnated with cast iron, iron oxides and components resultant from iron oxides interacting with the mixture.

Burnt-ons tend to be significantly thinner when activated graphites are used as coating filler (Table 4).

## Conclusion

The findings show that the sedimentation stability of suspensions and coatings is governed by the size of the electrical double layer in graphite particles. Due to mechanical activation, the electrical double layer of graphite grows from 0.3 to 0.4 mV, while the sedimentation stability after 24 h of settling rises from 66 to 76% and from 87 to 97% with the concentrations of graphite being 30 and 50 w/w per 100 w/w of water, correspondingly. Accumulation of structural defects in graphite particles contributes to the growth of the electrical double layer at the surface of graph-



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