$\begin{array}{c}\n \text{MINERAL MINING}\n \quad \text{TECHNOLOGY}\n\end{array}$

Usability of Chloride Mine Water in Preparing Cemented Paste Backfill

T. I. Rubashkina*^a* *** and M. A. Kostina***^a*

*a Belgorod State University, Belgorod, 308015 Russia *e-mail: korneychuk@bsu.edu.ru*

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Abstract—The usability of salt mine water with high content of chloride-ions in preparing cemented paste backfill is studied. The rheological and mechanical properties of experimental backfill mixtures at different cement consumption are analyzed at uniform and compound aggregate hydrated with tap and mine water with the content of chloride-ions up to 0.75% of the mass of cement. The strength, elasticity modulus and Poisson's ratio are calculated in cemented paste backfill with tap and mine water after curing for 28, 60, 90 and 360 days. It is found that the strength, elasticity and deformation characteristics of the test cemented paste backfill made of mine water change similarly to the backfill made of tap water, at deviation of $\pm 10\%$ and ±4% in terms of strength and deformation, respectively. Chloride-ions contained in mine water have no adverse effect on rheological properties of backfill or hydrated cement, and on dynamics of development of strength in the mixture.

Keywords: Cemented paste backfill, mixing water, salt mine water, uniaxial compression strength, static elasticity modulus, Poisson's ratio.

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INTRODUCTION

Mine water is water that collects in mines as a result of groundwater and surface water inflows and gets polluted during various mining operations. Mine water becomes impure with mostly fine suspended particles of minerals and enclosing rocks during drilling and blasting, heading and stoping, loading and transportation. Furthermore, because of high-level mechanization of mining operations, mine water is contaminated with petrochemicals and can experience bacterial contamination due to decay of timber structures (mine support, partitions, etc.). Chemical composition of mine water depends on geological and geotechnical factors, and on the depth of mineral occurrence. Physicochemically, mine water can be acidic, mineralized and purified with suspended rock particles. Mine water contains ions of iron, aluminum, silicon, calcium, magnesium, chloride, zinc, copper, SO_4^{-2} , HCO³⁻, H⁺, as well as bacteria at different ratios. Water flow velocity and stagnation in roadways, and the mining depth govern mine water aggressiveness which is estimated by concentration of hydrogen ions (pH). Acidic water is the most aggressive water [1].

Each mine develops and implements different complex and expensive measures aimed at removal of mine water to ground surface and at water purification before recycling or discharge to surface water bodies. Purification of mine water with higher contents of impurities includes water settling in storage ponds, acidic water undergoes neutralization, and highly mineralized water is subjected to demineralization. Purified mine water can be used in mines for dust suppression by means of water injection in minerals, or for sprinkling, main roof rock softening, hydrotransport of mineral and waste rock, backfilling and mineral processing [2, 3].

Recycling of highly mineralized mine water is limited because of the high content of different cations and anions (Na, K, Ca, Mg, Fe, CI, SO4 etc.), which exceeds the maximum allowable concentrations even for process water and makes the mineralized water inapplicable even for preparation of cemented paste backfill.

First, water for the production of cemented paste backfill (using concrete, cement grouts, etc.) is an active component intended to ensure concreting, spreadability and placeability of the ready mix. The mixing water quality is evaluated in terms of the content of contaminants which can impede normal setting and hardening of a binder, or can initiate hardened pockets in the mix structure, which reduce the strength and durability of the mix, and can corrode steel rods. The most harmful impurities in water are soluble salts containing sulfate ions SO_4^{-2} and chloride ions Cl^{-1} which readily react with calcium hydroxide Ca(OH)₂ generated during cement hydration. New compounds appear as a result, either water-soluble (e.g. calcium chloride CaCl₂), or weak and loose, or crystallizable at a substantial change in volume (calcium sulfate CaSO4). These process can run simultaneously sometimes. All processes lead to the chemical corrosion of cement stone. Moreover, soluble salt of high concentration crystallizes in pores of cement stone and form blooms on the surface of hardened cement.

Second, the increased content of sulfate ions and chloride ions in water (more than 1% of the mass of cement) promote chemical corrosion of steel rods in concrete [4–6]. Corrosion affects the physical and mechanical properties of concrete and alter the stress–strain behavior of the concrete structures [7–10].

Cemented paste backfill with a cement binder, despite common patterns of cement stone formation and strength development with concrete, has its specificity and differences from concrete, which prevents from the univocal assumption of the above-described studies. Unlike concrete, cemented paste backfill is unnecessary to have such high strength and excellent appearance, which tolerates the use of low-grade aggregates and cement, or production waste, as well as allows a higher (more than 1) water/cement ratio to increase flowability and placeability of a backfill mix, and enables its transportability to mined-out voids in pipelines by gravity for long distances (to 3–5 km). Such backfilling needs no reinforcement over the whole volume of backfill, and features no special standards on blooms on the backfill surface if they induce no corrosion of the cemented paste backfill.

Highly mineralized mine water can be used effectively in preparation of different-composition backfill mixtures for operation in different geological conditions [11–13]. In this case, the backfill efficiency is governed by its ability to preserve strength and deformability for a long time (not less than a year).

This study aims to analyze applicability of highly mineralized mine water with a high content of chloride ions as a mixing water in manufacture of cemented paste backfill.

1. RESEARCH PROCEDURE

The tests were carried out with the selected compositions of backfill mixtures at different consumptions of Portland slag cement TSEM II/А-Ш 32.5 N class 32.5, and at different consumptions and compositions of an aggregate—uniform (low-grade natural very fine sand with increased clay content) and granulated furnace slag of optimized coarseness by screening up to a size of 0–5 mm [14, 15], which ensure the cemented paste backfill strength of not lower than 10 MPa within a conventional time of undermining (60 days).

		Hydrogen index pH			
Water	Ions SO_4^{-2} Ions $Cl-1$ Soluble salt Suspended particles				
Mine water	10450	57 ± 17	> 5000	8 ± 1	7.4 ± 0.2
Tap water	454	119 ± 30	221.6 ± 19.9	7 ± 1	7.4 ± 0.2
GOST-set MAC for manufacture of unreinforced concrete structures free from boom standards	10 000	2.700	4.500	300	$4.0 - 12.5$

Table 1. Contents of soluble salt, sulfates, chlorides and suspended particles in mine and tap water

The mixing water was highly mineralized mine water in the quantity sufficient for the production of fluid mixtures with the spreadibility not less than 220 mm on Suttard viscometer. Also, the same mixtures were prepared using tap water. The mixtures with tap water were assumed as the reference compositions in the tests of the high-mineralized chloride water effect on the physical and mechanical properties of cemented paste backfill.

The prepared backfill samples were cubes $100\times100\times100$ mm and cylinders with a height/diameter ratio of 2:1 in amount sufficient for the uniaxial compression and deformation tests (elasticity modulus, Poisson's ratio) in the static mode at the normal curing age of 28, 60, 90 and 360 days, at a temperature of 20 ± 2 °C and a relative air humidity of 95 \pm 5%.

Preliminary, the qualitative chemical analysis of the test mineralized water, tap water and aggregates was carried out. Table 1 describes the compositions of the highly mineralized and tap water as per the state standard GOST 23732-2011 Water for Concretes and Mortars, Specifications for manufacture of unreinforced concrete structures.

The comparative analysis of the data in Table 1 shows that the test water is highly mineralized and contains sulfate ions SO_4^{-2} and chloride ions Cl^{-1} in concentrations exceeding the maximal allowable concentrations set by the state standard GOST 23732-2011 for unreinforced concrete structures by 4.5 and 11.0%, respectively. The dominant anion (Cl^{-1}) makes it possible to assume the water as chloride water. The other indicators arte within the maximal allowable values. The quantitative chemical analysis of aggregates represented by very fine natural sand and granular furnace slag 0–5 mm in size is presented in Table 2.

Chemistry of sand and slag differs in the contents of $SiO₂$, CaO, sulfates and sulfides, while the content of chloride ions in the same and is 0.02% by mass. The content of chloride ions in the aggregates was included in the calculation of their total content in the backfill mixture. Table 3 describes the physicotechnical properties of the aggregates. The test sand has a very low fineness modulus (0.02) due to the domination of flour particles (smaller than 0.16 mm) and owing to the increased content of clayey particles in its grain composition. The screened granular furnace slag has the characteristics of coarse sand and is free from clayey components. Both sand and slag have similar values of the true and bulk specific gravities, which simplifies selection of compositions of directionless backfill mixtures.

Aggregate	\sim 1- ◡ェ	ມ	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	Na ₂ O	MgO	K_2O	TiO ₂	MnO
Sand	0.02	0.03	94.30	3.20	0.92	0.18	0.00	0.10	0.85	0.63	0.01
Slag	0.02	0.31	27 '.28	10.29	0.13	37.41	0.67	12.30	0.53	0.46	0.43

Table 2. Chemistry of aggregates, % by mass

Aggregate						Oversize, % by mass, at given screen aperture, mm	Fineness	Content of clayey	True / bulk specific	
	2.50	1.25	0.63	0.315	0.16	< 0.16	modulus	and flour particles, %	gravity, kg/m ³	
				Partial						
Sand			0.06	0.18	1.66	98.10	0.02	7.37	2675/1630	
				Total		Very fine				
			0.06	0.24	1.90					
				Partial						
Slag	2.07	10.63	52.35	24.40	6.39	4.15	2.65	0.00	2700/1490	
				Total		Coarse				
	2.07	12.70	65.06	89.46	95.85					

Table 3. Physicotechnical properties of sand and screened furnace slag

The experimental compositions of cemented paste backfill: three compositions with mixing mine water MW (1-0SH-MW, 2-25SH-MW, 3-40SH-MW) and mixing tap water TW (1-0SH-TW, 2-25SH-TW, 3-40SH-TW), the densities, spreadabilities at Suttard viscometer, as well as the total mixture contents of chloride ions in percent by mass of cement are described in Table 4.

The cement consumption per 1 $m³$ of the experimental backfill mixture varies from 490 kg with the natural very fine sand as an aggregate to 380 kg with the optimized coarseness aggregate (Table 4). The rheological properties of the cemented paste backfill made of both tap water (1-0SH-TW, 2-25SH-TW, 3-40SH-TW) and mine water (1-0SH-MW, 2-25SH-MW, 3-40SH-MW) fit the experimental conditions—spreadability not less than 220 m at Suttard viscometer. Slight differences in the spreadability of the experimental and reference compositions are due to varied content of clayey particles in sand. In the composition manufactured at the minimal cement consumption, the water/cement ratio is higher (1.2), and the total content of chloride ions in percent by mas of cement is higher, too. The total content of chloride ions in the mine water-based compositions is 9–11 times higher than their content in the reference compositions.

			Consumption per 1 m^3		Total				
Mixture			Aggregate			W/C	Density, kg/m^3	Spreadability,	content of chloride ions, $%$ by mas of cement
	Sand, $\frac{0}{0}$	Slag, $\frac{0}{0}$	Fineness modulus	Clay content, %	Cement, kg			mm	
$1-0$ SH-TW	100	$\overline{0}$	0.02 Very fine	7.37	490	1.1	1790	221	0.06
$1-0$ SH-MW	100	$\boldsymbol{0}$	0.02 Very fine	7.37	490	1.1	1790	223	0.69
$2-25SH-TW$	75	25	0.68 Very fine	5.53	430	1.1	1870	220	0.07
2-25SH-MW	75	25	0.68 Very fine	5.53	430	1.1	1870	221	0.71
3-40SH-TW	60	40	1.07 Very fine	4.42	380	1.2	1920	220	0.08
3-40SH-MW	60	40	1.07 Very fine	4.42	380	1.2	1920	224	0.75

Table 4. Sample backfill compositions

During the test periods of 28, 60, 90 and 360 days, the samples were tested on measurement machine ASIS-2017 for determining the uniaxial compressive strength, and the longitudinal and lateral deformations in compression in order to find the elasticity modulus and Poisson's ratio in the static mode. Before and after testing, the samples were visually inspected to detect blooms and visible chemical corrosion sites.

2. RESULTS AND DISCUSSION

The visual inspection of the samples before and after testing detected no visible corrosion of cement stone, and the mine water-based samples physically had no difference from the reference samples, neither by color nor by structure. After processing of the testing results, the uniaxial compressive strengths, static moduli of elasticity and Poisson's ratios of the cemented paste backfill mixtures made of mine and tap water after curing for 28, 60, 90 and 360 days are compiled in Table 5.

The test data analysis shows that the strength of the cemented paste backfill samples made of mine water differs from the strengths of the reference (tap water) samples by -0.3 to 1.4% at the age of up to 90 days and by $\pm 10\%$ at the age of 360 days (Table 5). In case of the experimental composition with the maximum cement consumption (490 kg) and with a uniform aggregate (100% sand), the tap water samples (1-0SH-TW) have the strength higher by 10.4% than the mine water samples have (Fig. 1a). In case of the experimental composition with the minimal cement consumption (380 kg) and with an optimized aggregate (60% sand, 40% slag), the mine water samples (3-40SH-MW) at the age of 360 days have the strength higher by 9.3% (Fig. 1b).

		28 days		60 days		90 days	360 days			
Composition	Value	Deviation, $\frac{0}{0}$	Value	Deviation, $\frac{0}{0}$	Value	Deviation, $\frac{0}{0}$	Value	Deviation, $\frac{0}{0}$		
				Uniaxial compressive strength, MPa						
$1-0SH-TW$	8.58		10.54		11.58		21.43			
$1-0$ SH-MW	8.64	-0.28	10.62	-0.30	11.67	-0.28	19.20	-10.40		
$2-25SH-TW$	8.53		10.48		11.51		18.50			
$2-25SH-MW$	8.56	0.40	10.52	0.43	11.56	0.43	16.72	4.20		
$3-40SH-TW$	8.48		10.42		11.45		17.96			
3-40SH-MWB	8.93	1.35	10.97	1.30	12.06	1.40	19.63	9.30		
		Elasticity modulus, GPa								
$1-0SH-TW$	2.98		3.07		3.13		3.58			
$1-0$ SH-MW	2.96	-0.09	3.09	0.56	3.14	0.55	3.46	-3.08		
$2-25SH-TW$	2.95		3.07		3.12		3.43			
$2-25SH-MW$	2.95	0.15	3.06	0.14	3.13	0.14	3.38	-1.26		
3-40SH-TW	2.98		3.09		3.15		3.40			
3-40SH-MW	3.00	0.45	3.17	2.53	3.17	0.43	3.49	2.63		
					Poisson's ratio					
$1-0SH-TW$	0.38		0.38		0.34		0.29			
$1-0$ SH-MW	0.39	2.63	0.39	2.63	0.35	2.94	0.30	3.45		
2-25SH-TW	0.38		0.37		0.33		0.26			
2-25SH-MW	0.38	0.00	0.37	0.00	0.34	3.03	0.27	3.85		
3-40SH-TW	0.38		0.37		0.33		0.25			
3-40SH-MW	0.38	0.00	0.38	2.70	0.34	3.03	0.26	4.00		

Table 5. Uniaxial compressive strengths, elasticity moduli and Poisson's ratios of experimental backfill compositions made of mine and tap water

Fig. 1. Strength of experimental cemented paste backfill at different ages: (a) maximal consumption of cement (490 kg) and uniform aggregate (100% sand), with tap water (1-0SH TP) and mine water (1-0SH-MW); (b) minimal consumption of (380 kg) and optimized aggregate (60% sand and 40% slag), with tap water (3-40SH-TW) and mine water (3-40SH-MW).

The experimental mixtures only differ by qualitative composition of mixing water. For this reason, the cause of a decrease or an increase in the strength may only be chemical processes during hydration of cement, and during formation and strengthening of cement stone. Possibly, addition of the aggregate with slag containing 30–40% of calcium oxide (Table 2) results in formation of some calcium chloride CaCl₂ in the cement–mine water system. In concrete technology, calcium chloride is used to intensify hardening and strength development in cement stone. This is a supposition, though. The practice of concrete technology tolerates the strength loss not higher than 15% [16].

The analysis of the results shows that the elasticity modulus in cemented paste backfill with mine water increases in proportion to the strength growth within the whole test period, and differs from the reference mixtures with tap water by -3.08 to 2.63%, or by $\pm 3\%$ at the average. At the age of 360, the experimental mixture with the maximal consumption of cement (490 kg) and with the uniform aggregate (100% sand) has the elasticity modulus higher by 3.08% in the samples with tap water (1-0SH-TW) than in the samples with mine water, while the experimental mixture with the minimal consumption of cement (380 kg) and with the optimized aggregate $(60\%$ sand, 40% slag) has the elasticity modulus higher by 2.63% in the samples with mine water (3-40SH0MW) than in the reference backfill samples. The difference in Poisson's ratios of the samples with tap water and mine water is insignificant within the test period, and is not higher than 4%, which is inside the experimental error limits.

CONCLUSIONS

It has been found that chloride ions present in mine water, used in manufacture of cemented paste backfill, in amount of 0.75% of mess of cement has no adverse effect on the rheology of the backfill mixture, on the cement stone formation and on the dynamics of strength development in the ready mixture. The strength, elasticity and deformation characteristics of the hardened experimental samples with mine water change similarly to the samples with tap water within the test period of 360 days, at differences of $\pm 10\%$ in terms of strength and $\pm 4\%$ in terms of deformation, which is allowable.

It is possible to use highly mineralized chloride mine water as a mixing water in manufacture of cemented paste backfill free from reinforcement after preliminary testing of specific compositions.

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