

STANISŁAW STRYCZEK *, BARBARA HLINIAK *

INFLUENCE OF BRINE ON RHEOLOGICAL PARAMETERS OF SEALING SLURRIES

WPŁYW SOLANKI NA PARAMETRY REOLOGICZNE ZACZYNÓW USZCZELNIAJĄCYCH

The rheological parameters of sealing slurries are a significant technological factor in the geoengineering works performed to seal and strengthen the soil and rock mass.

The paper presents the results of laboratory analyses of sealing slurries based on various cements and base fluids. The applied cements were selected in view of different C₃A content (a phase significantly influencing the rheology of fresh cement slurries).

With the elaborated results of laboratory analyses it will be possible to prognose the rheological properties of cement slurries, depending on the chemical and mineral composition of cements and chemical composition of base fluids.

Key words: rheology, sealing slurries.

W pracach geoinżynierijnych, a zwłaszcza typu otworowego związań z uszczelnianiem i wzmacnianiem ośrodka gruntowego i masywu skalnego bardzo ważnym parametrem technologicznym stosowanym do tego celu zaczynów uszczelniających są jego parametry reologiczne.

W artykule przedstawiono wyniki badań laboratoryjnych zaczynów uszczelniających sporządzonych na różnych rodzajach cementów oraz cieczy zarobowych.

Badania właściwości reologicznych świeżych zaczynów uszczelniających, a zwłaszcza typu cementowego wykazały, że zależą one od wielu czynników, do których należą:

- powierzchnia właściwa oraz granulacja nieorganicznych spojw hydraulicznych wchodzących w skład zaczynu uszczelniającego,
- iloraz wody i spojwa hydraulicznego (współczynnik w/s),
- skład chemiczny spojwa hydraulicznego (np. cementu),
- skład chemiczny cieczy zarobowej,
- obecność i skład chemiczny dodatków wchodzących w skład receptury zaczynu,
- sposób i dynamika (czas i szybkość) mieszania zaczynu,
- temperatura zaczynu,
- szybkość hydratacji,
- warunki i sposób pomiaru.

* WYDZIAŁ WIERTNICTWA, NAFTY I GAZU, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

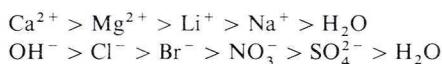
Stosowane cementy dobrano pod kątem różnej zawartości C₃A jako fazy, która w istotny sposób wpływa na reologię świeżych zaczynów cementowych.

Jednym z istotniejszych problemów w geoinżynierii otworowej jest odpowiedni dobór rodzaju oraz parametrów reologicznych zaczynu uszczelniającego górotwór solny. Do tego rodzaju prac stosuje się zaczyny uszczelniające tzw. solankowe sporządzane na osnowie solanki o pełnym nasyceniu.

Wpływ chlorku sodu jako zazwyczaj głównego składnika cieczy zarobowej do sporządzania solankowych zaczynów cementowych jest zróżnicowany w zależności od jego koncentracji i temperatury zaczynu.

Sole chlorkowe wpływają w sposób istotny na właściwości reologiczne zaczynów poprzez ich wpływ na szybkość wiązania. Przyspieszające działanie wiązania zaczynów cementowych zależy od wartościowości jonów zawartych w solance. Jest ono większe przy przejściu z jedno- do dwóch wartościowych jonów.

Zauważa się, że kationy i aniony w zależności od ich efektywności przyspieszającego działania na zaczyny sporządzane z cementów portlandzkich mogą być uszeregowane w następującej kolejności:



NaCl działa jako przyspieszacz czasu wiązania zaczynu przy koncentracji do 10% (wagowo w stosunku do masy cieczy zarobowej). Przy koncentracji między 10% a 18% NaCl, jego oddziaływanie na czas wiązania jest praktycznie niewidoczne i uważa się, że czas początku wiązania jest podobny do tego, jaki uzyskuje się przy stosowaniu wody pitnej jako cieczy zarobowej. Przy zawartości NaCl w cieczy zarobowej powyżej 18% (wagowo), oddziałuje on jako opóźniacz czasu wiązania zaczynów cementowych.

Opracowane wyniki z badań laboratoryjnych pozwolą na prognozowanie właściwości reologicznych zaczynów cementowych w zależności od składu chemicznego i mineralnego cementów oraz składu chemicznego cieczy zarobowej.

Słowa kluczowe: zaczyny solankowe, reologia.

1. Introduction

Rheological properties of fresh sealing slurries are of special interest mainly due to their relation with the radius of propagation of the slurry in a porous medium when applying one of geoengineering methods, i.e. pressure injection.

Sealing slurries used for this type of work are concentrated dispersion systems containing solid particles with strongly developed specific surface. These systems are complex as far as their physico-chemical properties go, therefore their rheological behaviour is also complicated. The analysis of factors influencing the rheological properties of sealing slurries is additionally hindered by continuous hydration of inorganic hydraulic binders [Kurdowski, 1991; Stryczek, 1997, 1998 b].

The complexity of the inorganic hydraulic binder-base fluid system makes the interpretation of rheological measurements obtained by numerous authors very difficult. This is mainly due to the fact that different methods had been used

(preparation of samples, dynamics of mixing, speed of coagulation) and changes in phase composition during hydration [Grzeszczuk, 1988, 1991, 1999].

The analysis of rheological parameters of fresh sealing slurries, especially the cement-base ones shows that they depend on a number of factors [Grzeszczuk, 1991; Hliniak, 1999; Kurodowski, 1991; Stryczek, 1997, 1998a, 1998b] e.g.:

- specific area and granulation of inorganic hydraulic binders making up the sealing slurry;
- water-to-hydraulic binder ratio (w/c);
- chemical composition of hydraulic binder (e.g. cement);
- presence and chemical composition of additives making up the recipe of the slurry; way and dynamics of mixing of slurry (time and speed);
- temperature of slurry;
- rate of hydration;
- conditions and way in which measurement was made.

The suitable selection of the type and rheological parameters of sealing slurries in the conditions of a saline rock mass is one of the most important problems in hole geoengineering. This type of works are made with the use of brine-base sealing slurries made from a fully saturated brine.

2. Factors influencing the rheological properties of cement slurries

Bearing in mind the grain size of the hydraulic binder (cement), fresh sealing slurries can be treated as disperse systems. Cement grains undergo coagulation, forming a continuous coagulation structure at a certain amount of the solid phase. Products of hydration are often neglected in the simplified model of this structure. For this reason the rheological properties of the modelled structures do not correspond to the description based on the results of measurements of real systems.

The high reactivity of cement, especially clinker phase C_3A in the presence of base fluid, causes that all grains are covered with a gel composed of a mixture of hydrated calcium silicates and aluminosilicates [Bomble, 1980; Grzeszczuk, 1991; Stryczek, 1999].

The mutual mobility of cement grains is to a great extent a result of quantity and type of products formed in the initial part of the hydration. The chemical and mineral composition of non-hydrated cement grains influences the physico-chemical properties of the formed film of gel. The charge distribution on the surface of colloidal particles and the solid phase concentration determine the intergranular strengths, having an impact on the ordering of grains in the coagulation structure, and thus the behaviour of the slurry subjected to external forces.

The formation of a water layer with an ordered build of stable surface plays an important role in the formation of rheological properties of sealing slurries, especially of the cement-base one. The internal zone with an ordered build gradually passes into the transient zone where the solid particles of the base fluid are

distributed at random, to assume the form of external water solution [Grzeszczuk, 1988].

The size of the internal and transient zones determines the viscosity of the sealing slurry. Depending on the surface charge of the solid phase, the width of the diffusion layer and the forces acting on ions in the formed solution, change. Due to the high reactivity of cement phases in the presence of water, the rheological properties of the sealing slurry mainly depend on the type and quantity of products of binder (cement) hydration products (except for water-binder coefficient and hydraulic binder (cement) dispersion); the character of surfaces of clinker phases is of lesser importance.

Bearing in mind the above, sealing slurries can have various rheological properties. The flow curves are recoverable or can indicate a histeresis. This is mainly due to the fact that at shorter times of measurement, the destruction of the structure of the slurry dominates, whereas at longer times — we can observe its recovery. Thus, in fresh cement slurries the destruction processes overlap under the influence of coagulation in a viscometer. Besides, the structure is recovered by the products of hydration of cement grains.

2.1. Chemical composition of cement

The influence of chemical composition of cement on rheological properties of cement slurries has not been sufficiently explained yet. It is often believed that this impact is much less than the concentration of solid phase in the slurry and comminution of cement. The influence of chemical composition of cement can be observed in the case of a delayed hydration of aluminates by calcium sulfate. This process significantly influences the rheological properties of fresh cement slurries in the initial stages of hydration, causing variation of these properties in time [Grzeszczuk, 1988].

The rheological properties of sealing slurries in the initial period depend on the type and amount of hydration products C_3A [Grzeszczuk, 1991]. The increase of ettringite content in slurry results in the growth of the flow limit and plastic viscosity. As can be viewed in [Bombled, 1980], the ettringite morphology is directly influenced by $Ca(OH)_2$ and SO_4^{2-} content in the liquid phase of the slurry. This can be indirectly connected with alkalies in clinker and with the type of calcium sulfate added to regulate the binding and reactivity of phase C_3A . The differences in $Ca(OH)_2$ concentration in the cement slurry solution lead to the change of morphology of ettringite from fine-crystalline to great needle-shape crystals.

According to J. P. Bombled the flow limit for fresh cement slurry results from the overlapping of the influence of flocculation and activities delaying aluminates hydration by sulfates in the initial period. The influence of sulfates on rheological properties of cement slurries depends on their solubility and content in the solution, and also on C_3A phase content.

The addition of calcium sulfate increases the flow limit for slurries in the case of clinkers with low C_3A content, and lowers the limit at high C_3A content. The

lowered limit at increased C₃A contents takes place due to the reaction of aluminate with gypsum, delaying hydration of the phase in the initial period. At a low C₃A content the increase of flow limit and predominance of flocculation processes can be observed. The change of water-to-cement ratio or of cement specific surface does not significantly change the impact of C₃A content on the flow limit for the slurry.

The tests on the influence of various sulfates [B o m b l e d, 1980; G r z e s z - c z y k, 1991] on rheological properties of cement slurries showed that it depends on the cation type.

The greatest influence can be observed with cations delaying the hydration process (Pb²⁺ and Ba²⁺) and the smallest in the presence of their accelerating counterparts (Li⁺, Na⁺, K⁺).

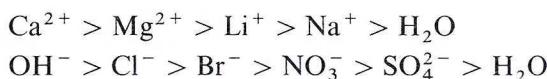
2.2. Type of base fluid

One of the most significant factors influencing the technological properties, in that rheological parameters of fresh cement slurries is the chemical composition of the base fluid.

The influence of sodium chloride, as a component of base fluid, varies depending on its concentration and temperature of the slurry.

Chlorides significantly influence the rheological properties of slurries through their effect on the speed of binding. The accelerating activity of cement slurries depends on the charge of ions in the brine. The acceleration increases with the increasing charge of ions (from one through three).

It has been observed that depending on their acceleration efficiency for slurries based on Portland cements, cations and anions can be ordered as follows [S t r y c z e k, 1997]:



NaCl acts as an accelerator of the time of binding of the slurry (to 10% of concentration by weight in relation to the mass of base fluid). At concentrations ranging between 10% and 18% NaCl, its impact on the time of binding is almost invisible and the time of beginning of binding is believed to be similar to the one which was obtained for drinking water as base fluid. At NaCl concentrations above 18% (wt.), it has a delaying effect on the time of binding of cement slurries.

3. Laboratory tests

The aim of the laboratory tests was to establish the influence of:

- water-to-cement ratio (w/c),
- chemical and mineral composition and their specific surface,
- chemical composition of base fluid,

— time of mixing
on rheological parameters of fresh sealing slurries based on cement.

The rheological properties of the analysed slurries were determined with the use of a Chan 35 API Viscometer (E, G and G Cahndler Engineering). The rotational speeds were: 600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1 rot/min which corresponds to the following speeds of coagulation: 1022, 511.02, 340.68, 170.34, 102.20, 51.10, 34.07, 17.03, 10.22, 5.11, 3.41 and 1.70 s^{-1} .

The following types of cement were used for sealing slurries:
 — Portland cement CEM I 42.5 from Cement Plant in Rejowiec,
 — Portland cement CEM I 32.5 R from Cement Plant in Górażdże,
 — metallurgical cement CEM III 32.5 NA from Cement Plant in Strzelce Opolskie.

The chemical and mineral composition of the cements used are listed in Table 1.

TABLE 1
Chemical and mineral composition of cements

Cement type	Specific surface [cm ² /g]	Density [g/cm ³]	Chemical composition of cement [%]								Mineral composition of clinker [%]				
			Losses due to baking	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
CEM I 32.5 R	3385	3.1	3.11	19.88	2.64	4.94	63.33	1.06	3.03	0.13	0.95	61.1	10.9	8.61	8.02
CEM I 42.5	3400	3.21	1.1	21.27	4.96	4.38	64.54	0.73	2.54	0.11	0.20	57.3	17.8	3.19	15.1
CEM III/A 32.5	3775	2.96	0.9	29.3	2.1	6.3	51.3	4.6	3.1	0.37	0.77	54.6	19.2	13.1	8.2

These cements were used for slurries having the water-to-cement ratio equal to 0.4, 0.5 and 0.6.

The following base fluids were used:

- tap water,
- artificial brine fully saturated with NaCl (20°C, 35.8 g NaCl/100 g H₂O),
- brine from Salt Mine „Wieliczka”:

NaCl	305 g/l	NH ₃	0.02 g/l
Ca ²⁺	1.05 g/l	HCO ₃ ⁻	0.21 g/l
Mg ²⁺	0.22 g/l	pH	7.5
SO ₄ ²⁻	6.33 g/l		

TABLE 2
Recipes for sealing slurries

Symbol of slurry	w/c	Base fluids			CEM I 32.5 R [%]	CEM I 42.5 [%]	CEM III/A 32.5 NA [%]
		Tap water	„Wieliczka” brine	Artificial brine			
RW4	0.4	×				100	
RW5	0.5	×				100	
RW6	0.6	×				100	
RS4	0.4			×		100	
RS5	0.5			×		100	
RS6	0.6			×		100	
RSW4	0.4		×			100	
RSW5	0.5		×			100	
RSW6	0.6		×			100	
GW4	0.4	×			100		
GW5	0.5	×			100		
GW6	0.6	×			100		
GS4	0.4			×	100		
GS5	0.5			×	100		
GS6	0.6			×	100		
GSW4	0.4		×		100		
GSW5	0.5		×		100		
GSW6	0.6		×		100		
SW4	0.4	×					100
SW5	0.5	×					100
SW6	0.6	×					100
SS4	0.4			×			100
SS5	0.5			×			100
SS6	0.6			×			100
SSW4	0.4		×				100
SSW5	0.5		×				100
SSW6	0.6		×				100

Cements designed for sealing slurries were sieved ($0.20\text{ mm} \times 0.08\text{ mm}$ square mesh) (PN-85/G-02320 Polish Standard „Cements and cement slurries for cementing operations in drilling wells”).

The temperature of the cements and base fluid is $22 \pm 2^\circ\text{C}$ (295 K).

The measured quantity of base fluid is poured into the cylinder and a high-speed electric mixer activated. The already weighed quantity of cement is added within the next 15 to 30 s. The time of mixing of slurries was about 3 min and the rotational speed of the mixer was about 1500 rot/min.

Thus prepared slurry was poured into a graded cylinder of the viscometer of the Chan-type. Having measured the rheological properties, the slurry was replaced in the cylinder and mixed (120 rot/min).

The rheological parameters of slurries were determined right after the base fluid was added, 1.5 hrs later and 3 hrs afterwards.

The recipes of the analysed sealing slurries are presented in table 2.

4. Discussion of the results

To determine the rheological parameters, the results obtained from the viscometer of the Chan-type were statistically analysed with the use of the least square method. An assumption was made that the sealing slurry can be described with the Bingham, Ostwald de Vaele and Casson models.

The degree of fitting of regression equations to measurement data for the individual models was determined from the correlation coefficients.

The results of calculations for each of the analysed model were presented in table 3.

Based on the values of the correlation coefficients (table 3), statistical analyses were made to determine the influence of the above mentioned factors w/c, type of cement and base fluid as well as time of mixing on the rheological model (best adjusted to the measurement data).

The Casson model turned out to be most suitable for the slurries with w/c equal to 0.4 and 0.6, slurries based on cement CEM I 42.5 (Rejowiec) and CEM III/A 32.5 NA (Strzelce Opolskie) and brine-based slurries (artificial and „Wieliczka” brines). With the time of mixing as a reference criterion, the best fitting was observed for the Casson model (both right after base material was introduced and also 1.5 and 3 hrs later).

In the case of the Ostwald de Vaele model, the best fit was obtained for slurries with w/c equal to 0.5, for slurries based on CEM I 32.5 (Góraždże) and tap water-base slurries.

The lowest correlation coefficients were obtained for the Bingham model. Hence the conclusion, the best fit to the rheological model was obtained for data from table 3 was obtained for the Casson model.

The influence of the water-to-cement ratio and the type of the base fluid on rheological properties of sealing slurries is presented in table 3 and figures 1 to 3.

TABLE 3

Rheological parameters of slurries

Symbol of slurry	w/c ratio	Time of mixing	Rheological model								
			Bingham			Ostwald de Vaele			Casson		
			Plastic viscosity [Pa]	Flow limit [Pa]	Correlation coefficient	Consistency coefficient [Pa s ⁿ]	Characteristic coefficient of flow [-]	Correlation coefficient	Casson viscosity [Pa s]	Flow limit [Pa]	Correlation coefficient
1	2	3	4	5	6	7	8	9	10	11	12
GW4	0.4	after base	0.2561	19.370	0.9788	8.1572	0.4897	0.9973	0.1718	8.195	0.9919
		1.5	0.2325	20.163	0.9384	9.3515	0.4778	0.9971	0.1543	10.907	0.9691
		3	0.3748	29.957	0.9349	13.652	0.4540	0.9966	0.2395	13.567	0.9746
GW5	0.5	after base	0.1156	9.897	0.9915	3.2548	0.5429	0.9975	0.0848	3.674	0.9941
		1.5	0.1082	11.267	0.9869	3.5726	0.5282	0.9975	0.0775	4.387	0.9899
		3	0.1037	11.599	0.9849	3.7490	0.5159	0.9981	0.0734	4.635	0.9893
GW6	0.6	after base	0.0447	5.328	0.9892	2.1304	0.4615	0.9949	0.0295	2.415	0.9943
		1.5	0.0413	5.218	0.9916	2.3028	0.4326	0.9890	0.0255	2.593	0.9917
		3	0.0394	5.535	0.9917	2.6624	0.3996	0.9877	0.0231	2.921	0.9937
GS4	0.4	after base	0.4914	23.216	0.9764	15.473	0.3924	0.9874	0.2595	12.397	0.9945
		1.5	0.3162	27.115	0.9496	13.363	0.4246	0.9961	0.1872	13.411	0.9766
		3	0.3153	27.742	0.9522	13.945	0.4163	0.9978	0.1826	14.048	0.9777
GSS	0.5	after base	0.2518	15.261	0.9891	6.5142	0.5158	0.9973	0.1736	6.166	0.9960
		1.5	0.1716	13.477	0.9814	5.7203	0.4846	0.9989	0.1122	5.936	0.9932
		3	0.1661	14.148	0.9764	5.9261	0.4779	0.9992	0.1075	6.319	0.9881
GS6	0.6	after base	0.0429	11.091	0.9873	6.6373	0.2801	0.9699	0.0192	7.218	0.9910
		1.5	0.0406	3.463	0.9984	1.8078	0.4387	0.9703	0.0265	1.643	0.9990
		3	0.0397	3.341	0.9988	1.8073	0.4318	0.9662	0.0256	1.615	0.9984

1	2	3	4	5	6	7	8	9	10	11	12
GSW4	0.4	after base	0.5348	21.993	0.9892	15.522	0.3934	0.9782	0.2836	11.747	0.9987
		1.5	0.3375	25.189	0.9601	12.277	0.4445	0.9976	0.2078	11.879	0.9839
		3	0.3782	24.952	0.9709	12.170	0.4601	0.9976	0.2376	11.438	0.9881
GSW5	0.5	after base	0.1997	14.109	0.9890	6.5698	0.4748	0.9960	0.1284	6.392	0.9946
		1.5	0.1175	14.263	0.9876	5.5725	0.4646	0.9966	0.0777	6.427	0.9930
		3	0.1103	11.024	0.9939	4.6313	0.4713	0.9926	0.0733	4.969	0.9958
GSW6	0.6	after base	0.0771	15.215	0.9364	5.7204	0.4198	0.9972	0.499	7.152	0.9777
		1.5	0.0499	4.616	0.9966	2.2382	0.4456	0.9788	0.327	2.144	0.9990
		3	0.0494	3.898	0.9985	1.9945	0.4537	0.9740	0.329	1.794	0.9989
RW4	0.4	after base	0.1071	14.579	0.9970	4.7795	0.4914	0.9979	0.0732	6.199	0.9834
		1.5	0.1146	19.503	0.9473	5.0617	0.5191	0.9940	0.0824	7.756	0.9640
		3	0.1111	20.070	0.9493	5.7861	0.4911	0.9938	0.0764	8.575	0.9644
RW5	0.5	after base	0.0536	8.169	0.9815	3.3618	0.4274	0.9949	0.0335	3.975	0.9910
		1.5	0.0570	9.020	0.9768	3.3641	0.4471	0.9935	0.0358	4.334	0.9791
		3	0.0550	9.147	0.9770	3.5284	0.3343	0.9917	0.0337	4.530	0.9789
RW6	0.6	after base	0.0206	2.492	0.9958	1.3052	0.3943	0.9741	0.0123	1.297	0.9987
		1.5	0.0275	3.740	0.9924	1.8471	0.3962	0.9860	0.0163	1.958	0.9970
		3	0.0268	3.435	0.9956	1.8325	0.3845	0.9780	0.0155	1.862	0.9968
RS4	0.4	after base	0.1297	13.539	0.9884	7.5975	0.3764	0.9899	0.0698	7.539	0.9956
		1.5	0.1123	12.954	0.9948	6.1402	0.4257	0.9861	0.0696	6.458	0.9958
		3	0.1083	12.940	0.9944	6.1561	0.4209	0.9859	0.0662	6.563	0.9943
RS5	0.5	after base	0.0618	9.514	0.9904	4.8195	0.3753	0.9821	0.0356	5.125	0.9975
		1.5	0.0535	5.587	0.9976	2.9836	0.4076	0.9708	0.0330	2.842	0.9986
		3	0.0516	5.187	0.9979	2.7724	0.4123	0.9715	0.0320	2.623	0.9988

1	2	3	4	5	6	7	8	9	10	11	12
RS6	0.6	after base	0.0269	2.323	0.9984	1.2356	0.4329	0.9702	0.0172	1.130	0.9982
		1.5	0.0256	2.173	0.9981	1.1164	0.4436	0.9727	0.0167	1.028	0.9982
		3	0.0251	2.055	0.9986	1.0985	0.4386	0.9672	0.0163	0.982	0.9982
RSW4	0.4	after base	0.1141	12.275	0.9952	5.6967	0.4389	0.9868	0.0725	5.936	0.9965
		1.5	0.1117	12.429	0.9952	5.9401	0.4284	0.9866	0.0692	6.215	0.9953
		3	0.1083	12.940	0.9944	6.1561	0.4209	0.9859	0.0662	6.563	0.9943
RSW5	0.5	after base	0.0516	10.844	0.9964	6.9082	0.2827	0.9497	0.0239	6.995	0.9956
		1.5	0.656	6.073	0.9984	3.2695	0.4211	0.9701	0.0413	3.026	0.9984
		3	0.0638	5.598	0.9981	2.8991	0.4374	0.9720	0.0415	2.654	0.9990
RSW6	0.6	after base	0.0247	4.638	0.9989	3.1121	0.2794	0.9214	0.0116	2.994	0.9927
		1.5	0.0268	2.087	0.9986	1.0885	0.4503	0.9686	0.0178	0.965	0.9984
		3	0.0262	2.026	0.9989	1.0870	0.4449	0.9660	0.0172	0.953	0.9982
SW4	0.4	after base	0.4125	17.830	0.9865	8.8448	0.5118	0.9922	0.2842	7.056	0.9974
		1.5	0.3522	25.436	0.9627	13.357	0.4253	0.9883	0.2139	12.194	0.9890
		3	0.7171	24.041	0.9849	15.145	0.4653	0.9916	0.4337	11.089	0.9970
SW5	0.5	after base	0.1121	14.986	0.9619	3.7212	0.5511	0.9982	0.0850	5.310	0.9775
		1.5	0.1066	13.698	0.9811	4.7880	0.4829	0.9976	0.0724	5.894	0.9874
		3	0.1140	13.658	0.9821	4.5170	0.5028	0.9984	0.0798	5.589	0.9883
SW6	0.6	after base	0.0538	6.772	0.9928	3.1571	0.4193	0.9884	0.0330	3.400	0.9960
		1.5	0.0458	6.707	0.9975	2.9455	0.4172	0.9916	0.0276	3.419	0.9905
		3	0.0489	6.380	0.9916	2.9755	0.4152	0.9902	0.0298	3.231	0.9956
SS4	0.4	after bas	0.6307	16.817	0.9915	10.425	0.5092	0.9952	0.4050	1.142	0.9981
		1.5	0.5223	21.521	0.9724	12.949	0.4485	0.9977	0.3053	10.339	0.9911
		3	0.5191	22.284	0.9701	13.380	0.4431	0.9971	0.2995	10.863	0.9888

1	2	3	4	5	6	7	8	9	10	11	12
SS5	0.5	after base	0.1235	12.031	0.9971	5.9181	0.4373	0.9818	0.0785	5.860	0.9971
		1.5	0.1064	7.809	0.9987	4.1226	0.4579	0.9758	0.0701	3.701	0.9970
		3	0.1026	8.307	0.9987	4.3449	0.4467	0.9754	0.0665	4.008	0.9969
SS6	0.6	after base	0.0586	7.054	0.9972	3.9161	0.3801	0.9652	0.0345	3.770	0.9989
		1.5	0.0502	3.827	0.9988	1.9894	0.4550	0.9733	0.0334	1.770	0.9986
		3	0.0474	3.984	0.9990	2.2165	0.4252	0.9630	0.0302	1.966	0.9980
SSW4	0.4	after base	0.6854	20.209	0.9895	12.656	0.4888	0.9942	0.4281	8.934	0.9979
		1.5	0.6530	24.526	0.9866	16.385	0.4273	0.9862	0.3685	12.286	0.9972
		3	0.7523	24.538	0.9890	16.009	0.4586	0.9895	0.4470	11.591	0.9974
SSW5	0.5	after base	0.1347	13.999	0.9953	6.4853	0.4431	0.9872	0.0868	6.640	0.9978
		1.5	0.1234	11.108	0.9973	5.3045	0.4543	0.9841	0.0806	5.214	0.9974
		3	0.1226	10.872	0.9977	5.3087	0.4508	0.9818	0.0799	5.127	0.9978
SSW6	0.6	after base	0.0519	7.089	0.9972	4.1037	0.3543	0.9583	0.0291	3.983	0.9984
		1.5	0.0441	3.867	0.9989	2.1379	0.4212	0.9629	0.0280	1.913	0.9983
		3	0.0445	3.832	0.9990	2.1349	0.4219	0.9625	0.0283	1.900	0.9981

As expected, the increment of the w/c ratio (and so lowering of cement concentration in slurries) leads to the lowered viscosity of slurries.

In the base of brines used as base fluids, a considerable increase of viscosity can be observed in comparison to slurries based on tap water.

As already mentioned, the initial stage of hydration of cement is mainly connected with the phase C₃A, and the rheological parameters of slurries in the initial stage depend on the type and quantity of products of hydration of C₃A.

The influence of the cement type (and so the aluminates content) on rheological properties of slurries was presented in figures 4 to 6.

The highest value of plastic viscosity (regardless the base fluid used) was obtained by slurries based on metallurgical cement CEM III/A (3.1% C₃A in clinker), lower values for slurries based on Portland cement CEM I (Górażdże) with 8.6% C₃A content. Slurries based on Portland cement (Rejowiec) with low aluminates content in clinker (3.19% of C₃A) had the lowest values of plastic viscosity.

The rheological properties of slurries is also significantly influenced by the specific surface of the cements used.

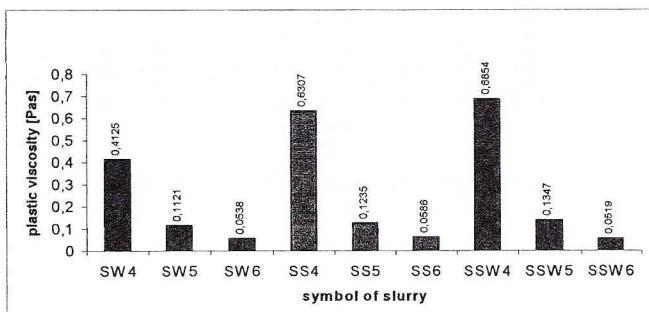


Fig. 1. Change of plastic viscosity of slurries based on cement CEM III/A, depending on the type of base fluid and w/c ratio: 1 — plastic viscosity, 2 — symbol of slurry

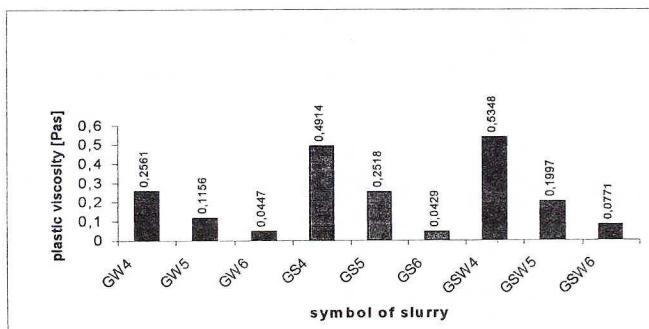


Fig. 2. Change of plastic viscosity of slurries based on cement CEM I 32.5, depending on the type of base fluid and w/c ratio

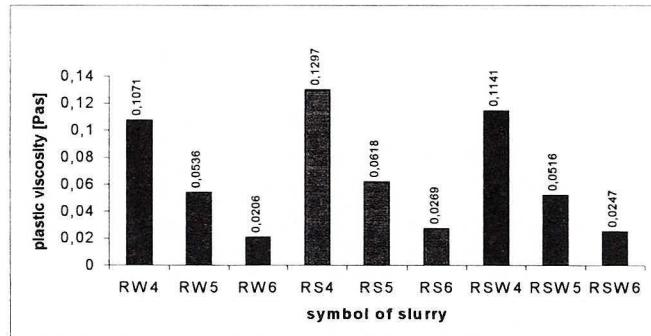


Fig. 3. Change of plastic viscosity of slurries based on cement CEM I 42.5, depending on the type of base fluid and w/c ratio

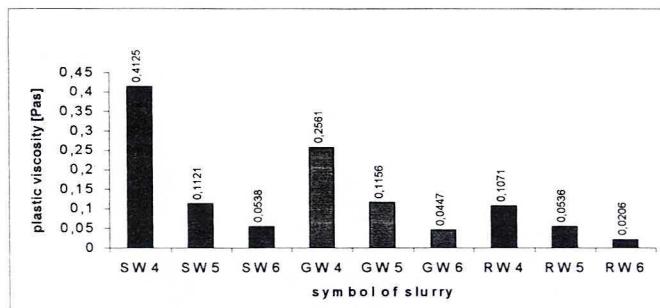


Fig. 4. Change of plastic viscosity of slurries based on tap water, depending on the type of base fluid and w/c ratio

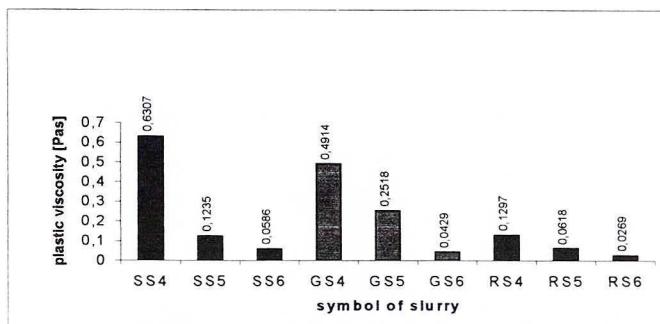


Fig. 5. Change of plastic viscosity of slurries based on artificial brine, depending on the type of base fluid and w/c ratio

Based on the analyses, slurries based on metallurgical cement CEM III/A with specific surface equal to $3775 \text{ cm}^2/\text{g}$ had a higher viscosity as compared to the slurries based on Portland cements (specific surface CEM I 32.5 — 3385; CEM I 42.5 — $3400 \text{ cm}^2/\text{g}$).

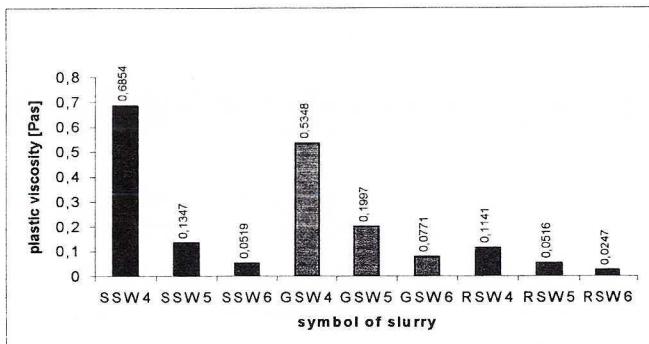


Fig. 6. Change of plastic viscosity of slurries based on „Wieliczka” brine, depending on the type of base fluid and w/c ratio

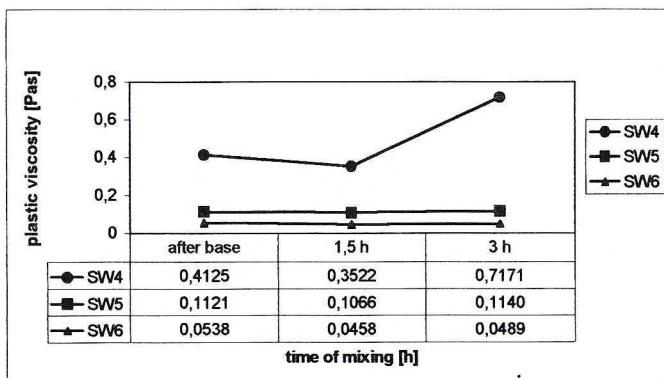


Fig. 7. Change of plastic viscosity of slurries during mixing (CEM III/A, tap water): 1 — plastic viscosity, 2 — time of mixing

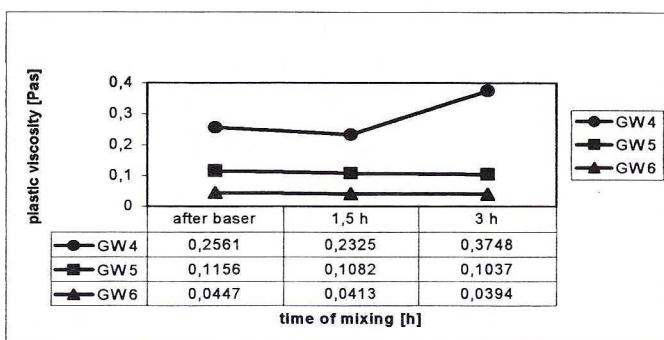


Fig. 8. Change of plastic viscosity of slurries during mixing (CEM I 32.5, tap water)

The graphs 7 to 15 show the changes of plastic viscosity of slurries based on tap water (Figs 7 to 9), artificial brine (Figs 10 to 12) and „Wieliczka” brine (Figs 13 to 17), accounting for the time parameter as relevant in geoengineering technologies.

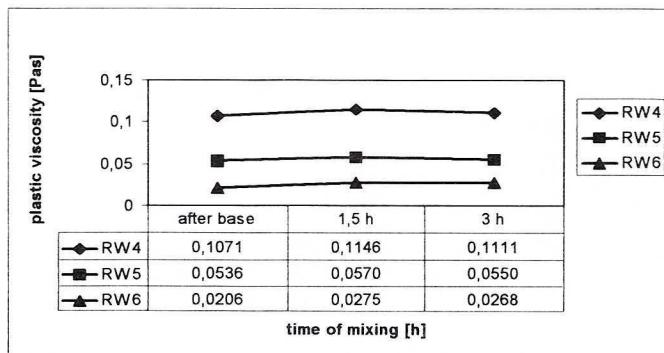


Fig. 9. Change of plastic viscosity of slurries during mixing (CEM I 42.5, tap water)

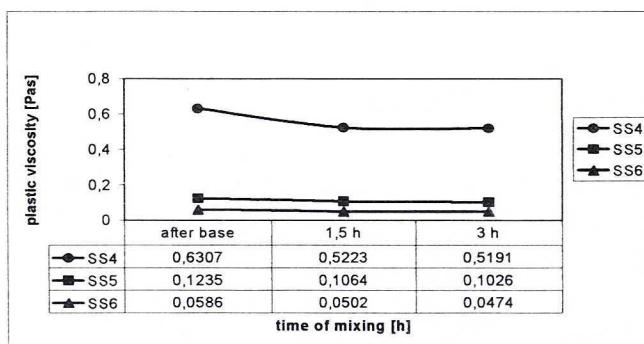


Fig. 10. Change of plastic viscosity of slurries during mixing (CEM III/A, artificial brine)

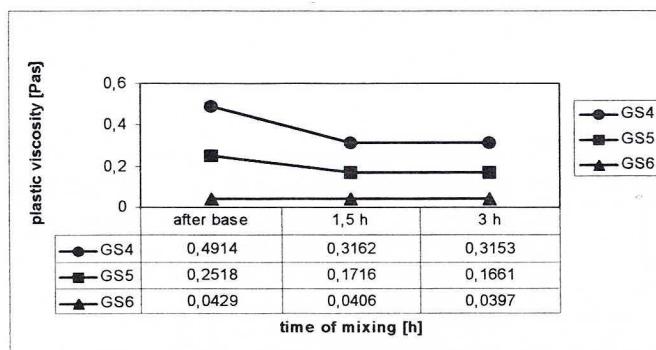


Fig. 11. Change of plastic viscosity of slurries during mixing (CEM I 32.5, artificial brine)

Based on the analysis of the obtained results, the plastic viscosity of slurries lowers to 3 hrs after base components had been introduced. Water-base slurries ($w/c = 0.4$) are an exception here (Figs 7 to 9). In this case the viscosity grows (3 hrs after base components had been introduced) and this is due to thickening of slurry (the so-called beginning of binding).

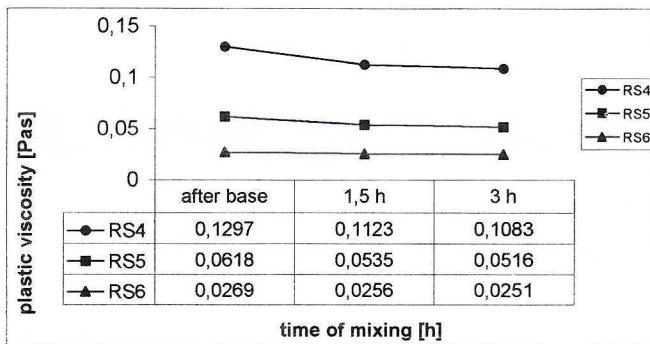


Fig. 12. Change of plastic viscosity of slurries during mixing (CEM I 42.5, artificial brine)

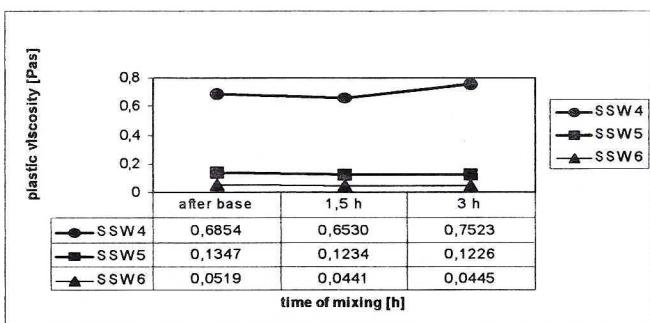


Fig. 13. Change of plastic viscosity of slurries during mixing (CEM III/A, „Wieliczka” brine)

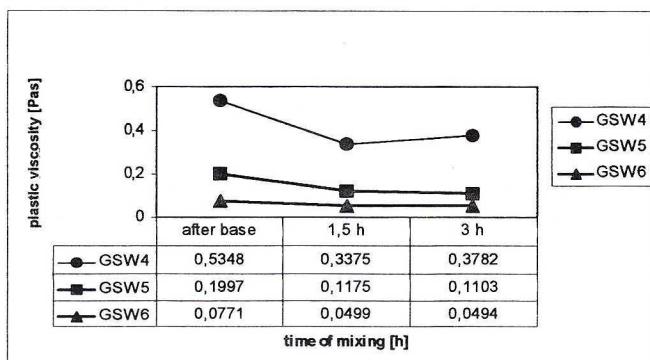


Fig. 14. Change of plastic viscosity of slurries during mixing (CEM I 32.5, „Wieliczka” brine)

Because of the influence of w/c ratio on the time of binding (delayed time of beginning of binding at w/c ratio increase), the slurries with higher water-to-cement ratio do not exhibit any growth of plastic viscosity 3 hrs after base components had been added.

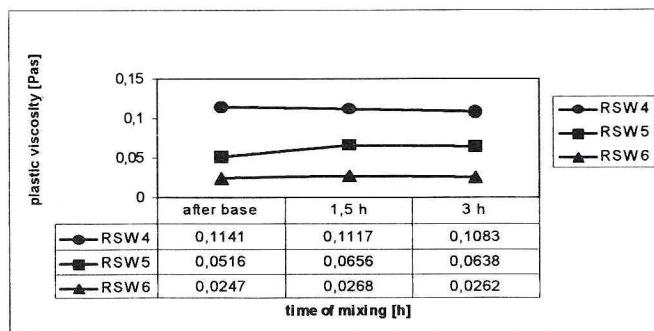


Fig. 15. Change of plastic viscosity of slurries during mixing (CEM I 42.5, „Wieliczka” brine)

In the case of brines used as base components (Figs 10 to 15), the lowered viscosity of slurries (to 3 hrs) is connected with the NaCl concentration in the base fluid. As already mentioned, chlorides significantly influence the rheological properties of slurries through their impact in the speed of binding.

At NaCl content in the base fluid > 18%, i.e. when brines are used, it delays the time of binding of sealing slurries.

5. Conclusions

1. Rheological parameters of sealing slurries significantly influence the selection of sealing technology and strengthening of soil and rock mass, saline rock mass including.
2. Rheological parameters of sealing slurries are significantly influenced by the water-to-cement ratio, specific surface, chemical composition of base fluid and cement.
3. The comparison of rheological parameters of the analysed slurries shows to the influence of brine, as a base fluid, on the type of rheological model and plastic viscosity of slurries.
4. Depending on definite geological-mining conditions, the sealing works should be made with regard to the suitable chemical and mineral composition of cements, in view of technological parameters prognosing for both fresh and hardened slurries.

Elaborated within Statute Researches No 11.190.01 University of Mining and Metallurgy, Cracow.

REFERENCES

- Bombled J. P., 1980. Influence of sulphates on the rheological behaviour of cement pastes and their evolution. Proc. 7th. Int. Congres on the Chemistry of Cement. Vol. III. s. VI—164. Paris.
 Grzeszczuk S., 1988. Wpływ alkaliów na właściwości reologiczne zaczynów cementowych. Cement, Wapno, Gips 8, 161—163.

- G r z e s z c z y k S., 1991. Właściwości reologiczne zaczynów cementowych, a skład klinkierów. Właściwości reologiczne świeżych zaczynów cementowych (część I). Cement, Wapno, Gips 8, 201—207.
- G r z e s z c z y k S., 1999. Wpływ wczesnych reakcji hydratacji na właściwości reologiczne zaczynów cementowych. Cement, Wapno, Beton 5, 180—184.
- H l i n i a k B., 1999. Rola faz glinianowych w zaczynach uszczelniających na przykładzie Kopalni Soli „Wieliczka”. Praca doktorska (w druku), Kraków.
- K e m b ł o w s k i Z., 1974. Reometria płynów nienewtonowskich. Wydawnictwo Naukowo-Techniczne, Warszawa.
- K u r d o w s k i W., 1991. Chemia cementu. Wydawnictwo Naukowe PWN, Warszawa.
- S t r y c z e k S., 1997. Prognosis of Binding Time for Saline Sealing Slurries. Archives of Mining Sciences, 42, 4, 555—565.
- S t r y c z e k S., 1998 a. Wpływ stopnia rozdrobnienia spoiw hydraulicznych na właściwości reologiczne zaczynów uszczelniających. Zeszyty Naukowe AGH. Górnictwo. Rok 22. Zeszyt 3. Kraków.
- S t r y c z e k S., 1998 b. Właściwości reologiczne solankowych zaczynów cementowo-bentonitowych. Technika Poszukiwań Geologicznych, Geosynoptyka i Geotermia, 3, Kraków.
- S t r y c z e k S., G o n e t A., R z y c z n i a k M., 1999. Technologia płuczek wiertniczych i zaczynów uszczelniających. Wydawnictwa AGH, Kraków.

REVIEW BY: DR HAB. INŻ. STANISŁAW WILK, KRAKÓW

Received: 14 December 1999.