

SECTOR A

SLOVAKIA DAYS – 21st – 23rd May, 2008

Paper A11

Corrosion protection aspects of some cementitious materials for the backfilling of casings

H.-G. Schöneich, E.ON-Ruhrgas AG, Essen, Germany

Abstract

During construction of pipelines cementitious materials are frequently proposed for backfilling of casings or microtunnels. Under service conditions the use of these materials shall not result in any impairment of corrosion protection effectiveness while following the technical rules with regard to coatings, cathodic protection and protection against alternating current corrosion. Considering this requirement the following characteristics of three cementitious backfilling materials had been investigated:

- resistivity as a function of time
- pH of pore liquid fluid
- polarisability of pipeline steel
- corrosion rate of pipeline steel at different adjustment of cathodic protection and under different levels of superposed alternating current

Useful indications can be concluded from the results of these investigations in order to select the appropriate backfilling material.

Korrosionsschutztechnische Eigenschaften einiger zementartiger Materialien für die Verfüllung von Mantelrohren

Zusammenfassung

Zementartige Materialien werden im Rohrleitungsbau häufig für die Verfüllung von Hohlräumen bei Mantelrohren oder Mikrotunneln vorgeschlagen. Es besteht an diese Materialien die Anforderung, dass ihr Einsatz unter Berücksichtigung der technischen Regeln für den passiven Korrosionsschutz, den kathodischen Korrosionsschutz und den Schutz gegen Wechelstromkorrosion zu keiner Beeinträchtigung der Korrosionsschutzwirkung führen darf. Vor diesem Hintergrund wurden für drei Verfüllmaterialien die folgenden Eigenschaften untersucht:

- Spezifischer Widerstand als Funktion der Zeit
- pH-Wert der Porenflüssigkeit
- Polarisierbarkeit von Rohrleitungsstahl
- Korrosionsgeschwindigkeit von Rohrleitungsstahl bei verschiedenen Einstellungen des kathodischen Schutzes sowie bei unterschiedlicher Wechselstromüberlagerung

Aus den gewonnenen Daten ergeben sich nützliche Hinweise für die Auswahl des geeigneten Verfüllmaterials.

Résumé

Lors de la construction de canalisations, des matériaux cimentaires sont régulièrement utilisés pour remplir des gaines ou des microtunnels. Dans des conditions de service, l'utilisation de ces matériaux ne devrait pas diminuer l'efficacité de la protection contre la corrosion à condition de respecter les prescriptions techniques relatives aux revêtements, à la protection cathodique et à la protection contre la corrosion par courant alternatif. Au vu de ces exigences, trois matériaux cimentaires de remplissage ont été testés au niveau des propriétés suivantes :

- Résistivité en tant que fonction du temps
- pH de suspension dans l'eau
- Polarisabilité de l'acier de la canalisation

• Taux de corrosion de l'acier de la canalisation à différents niveaux de réglage de la protection cathodique et à différents niveaux de courant alternatif superposé

Ces recherches ont livré des enseignements très utiles quant au choix du matériau de remplissage approprié.

Introduction

It is frequently proposed to use cementitious materials as a backfilling material for steel casings or microtunnels. From the point of view of the carrier pipe these materials must be compatible with the designed or applied corrosion protection concept:

- Compatibility with the coating material
- Compatibility with the cathodic protection system and the measures against alternating current corrosion

With regard to these requirements the properties of the backfilling material shall be as follows:

- The performance of the coating materials shall not be impaired by long term exposure to the backfilling material
- Effectiveness of cathodic protection may not be impaired
- The backfilling material shall not provoke an alternating current corrosion risk exceeding that from a "normal" soil.

No tests had been carried out to test the long term performance of polyethylene based coating materials (generally used in Germany) that is in contact with cementitious materials. It is believed that the corrosion system may be compared with buried fibre cement / polyethylene coated pipes, from which no damages have been reported up to now.

In order to characterize the cementitious materials resistivity and pH measurements had been performed. In order to test compatibility with the cathodic protection current density-potential-curves had been measured. Furthermore corrosion rate measurements (using electric resistance probes) under different adjustment of cathodic protection and superposed alternating current had been carried out. All potential values reported refer to the saturated Cu/CuSO₄-electrode.

Materials

The following cementitious materials were tested:

Material I

This material is a hydraulic setting backfill consisting of powdered calcareous marl and a cement according to EN 197.

Material II

This material is a hydraulic setting backfill consisting of powdered calcareous marl and a cement according to EN 197 but the fraction of binding material (cement) is reduced in comparison to material I, resulting in a reduced final strength.

Material III

This material is a hydraulic setting backfill consisting of powdered calcareous marl and a cement according to EN 197. Flue ash from a mineral coal operated power plant is added as filler material.

Results

Resistivity

The resistivity of the electrolyte solution which is in contact with the pipe steel surface within a coating holiday is an important parameter that determines the cathodic protection current density as well as the alternating current density under a given adjustment of the cp-system and high voltage interference situation.

Resistivity of materials was measured over 4 month using a slightly modified 4-pin Wenner-method (see fig. 1).



resistivity
$$\rho = 2 \bullet 2\pi a R$$

Fig. 1: Schematical drawing showing the experimental setup for resistivity measurements

Fig. 2: Results of resistivity measurements for three cementitious materials proposed for backfilling of casings

26.10.2001

15.11.2001

05.12.2001

06.10.2001

material I

material II material III

25.12.2001

Thin wires had been sticked into the bulk material and isolation was removed from their ends on a length of app. 4mm. Thus a factor 2 has to be introduced into the well known formula to calculate resistivity. This method makes results independent from surface effects, such as drying up.

Fig. 2 shows the results from the three test materials. Resistivity of the freshly prepared suspensions is app. $4\Omega m$. After 4 month resistivity of all materials is almost fixed, i. e. $70\Omega m$ for material I and app. $15\Omega m$ for materials II and III.

pН

The pH of an electrolyte solution is an important parameter that strongly determines the electrochemical behaviour of steel: pH>10 generally results in spontaneous passivation. Thus, in case of hydraulic setting cementitious materials it is useful to know the pH of the pore fluid after setting is completed.

Samples from materials I, II and III (after setting) had been reduced to small pieces (size < 1mm). A well defined quantity was stirred with 50ml deionised water for 10min. After this procedure pH was almost constant and measured using a calibrated glass electrode. Results are shown in fig. 3:



Fig. 3: Results from pH measurements with different cementitious test materials and mixtures with deionised water.

The pH of the pore fluid is estimated from extrapolation to 100%. Material I gives the highest pH (=12.4). pH of materials II and III is lower, which is in line with the lower fraction of binding material (material II) and the addition of flue ash (material III). Spontaneous passivation of steel, however, may be expected in either test material.

Polarization of steel

In case that cathodic protection is applied to the carrier pipe it is important to know the polarization of steel in contact with the cementitious material that is used for the backfilling of a casing.

Current density-potential-curves had been measured with steel probes (10cm²) in either test material covering the potential range between -1400mV and +800mV. A galvanostatically controlled current was applied between steel probe and a steel counter electrode. The relevant potential was generally measured after 30min. The IR-free potential of the steel probe was calculated from the polarization current and the electrolyte resistance between probe and the reference electrode. Current density-potential-curves had been measured 10 and 44 days after preparation of the test materials. Results are shown in fig. 4a (material I), 4b (material II) and 4c material III).

The results show similar characteristics for steel in either test material:

After 10 days cathodic polarization to U<-1000mV results from low current densities, i.e. < 0.1A/m². Cathodic polarization with 0.05A/m² was carried out over 12h yielding a distinctive potential shift to more negative potentials (e.g. fig. 4b) presumably resulting from the reduction of oxide surface layers. With increasing polarization the approximately logarithmic linear characteristic of the current density vs. potential indicates hydrogen evolution.





Fig. 4b:

Current density – potential curve for steel in cementitious material II (crossing of cathodic and anodic curves (after 10 days) results from non sufficient time allowing the probe to reach the rest potential after cathodic polarization)

Fig. 4c:

Current density – potential curve for steel in cementitious material III (crossing of cathodic and anodic curves (after 44 days) results from non sufficient time allowing the probe to reach the rest potential after cathodic polarization)

- Under anodic polarization all probes indicate the growth of an oxide layer in the potential range around -500mV followed by the potential shift into the oxygen evolution domain (at potential around +600mV).
- Interpretation of current density potential-curves that had been obtained after 44 days is very similar (in the meantime the probes were kept at rest potential, whereby a shift to more positive potentials between -600 and

-300mV) is observed. From the "shoulder" in the cathodic curve it may be again concluded that oxides need to be reduced before the potential reaches the hydrogen evolution domain. In either material the anodic current density needed to shift the potential into the oxygen evolution domain is lower (e.g. by an order of magnitude for material I) compared to the curve measured after 10 days.

From the results of these measurements no restrictions can be derived for the use of one of the materials as backfill in casings.

Corrosion measurements under simultaneous DC- and AC-load

These measurements had been carried out in order to characterize the three materials with regard to their "corrosiveness" to steel under different adjustments of cathodic protection and superposed alternating current. The experimental setup is schematically shown in fig. 5.



L x W x H = 30cm x 20cm x 18cm

Fig. 5:

Schematical drawing showing the experimental setup for corrosion experiments under simultaneous dc- and ac-load.

An electric resistance (ER-) probe (type "METRICORR", 1cm^2 , element thickness 500µm) was used to measure corrosion rate (twice per hour, accuracy better than 50µm/year). The dc-voltage between anode and ER-probe was controlled by a potentiostat. The ac-voltage (50Hz) was superposed using a transformer in series with the potentiostat. The probe potential and ac-voltage was measured with a calomel reference electrode.

The experimental design after filling the test materials into the vessels was as follows:

- ER-probe at rest potential over 10 days
- Loading with ac-current densities 30, 100, 200 and 500A/m² over 1-3 days for each load (phase I; see fig 6 and squares in fig. 7a, 7b, 7c)
- Loading with U_{on}=-1.27V (as a guidance level for the adjustment of the cathodic protection on-potential after the construction of a new pipeline [1]) and superposing an increasing ac-voltage: 0.5V, 0.85V, 2V, 3V, 6V, 15V over 1-10days for each set of parameters (the ac-voltage was not increased without adjusting the on-potential in case that the corrosion rate exceeded 0.1mm/a (phase II; see fig. 6 and open circles in fig. 7a, 7b, 7c)
- Depending on the result of the corrosion rate measurement the on-potential was shifted to more negative and/or positive level in order to show the impact

on corrosion rate at constant ac-voltage (phase III; see fig. 6 and full circles in fig. 7a, 7b, 7c).

As an example fig. 6 shows results for the remaining element thickness, the dccurrent density J_{dc} and the ac-current density J_{ac} from data logger measurements with material III. The corresponding data for on potential U_{on} and ac-voltage U_{ac} for this test as well as for measurements with materials II and III can be found in table 1. The corrosion rate v_{corr} was calculated from the slope of the diagram "remaining element thickness" vs. time.



Fig. 6: Results from data logger measurements with ER-probe in material III.

		material I					material II				material III					
date	parameter- variation	U.n	J _{do} (A/m²)	U	J_{ao} (A/m ²)	V₀₀rr (mm/a)	U.n	J_{d_0} (A/m ²)	U.,	J_{ao}	V _{oorr}	U.n	J_{d_0} (A/m ²)	U	J_{ao}	V _{oorr}
27.08.2007		-0.72	0.0	0.0	0	<0.05	-0.54	0.0	0.0	0	<0.05	-0.49	0.0	0.0	0	<0.05
28.08.2007		-0,52	0.0	0,0	0	<0,05	-0,45	0,0	0,0	0	<0.05	-0,40	0,0	0,0	0	<0.05
30.08.2007		-0,66	0,0	0,0	0	<0,05	-0,45	0,0	0,0	0	<0,05	-0,41	0,0	0,0	0	<0,05
31.08.2007		-0,64	0,0	0,0	0	<0,05	-0,48	0,0	0,0	0	<0,05	-0,42	0,0	0,0	0	<0,05
03.09.2007		-0,66	0,0	0,0	0	<0,05	-0,56	0,0	0,0	0	<0,05	-0,55	0,0	0,0	0	<0,05
05.09.2007		-0,65	0,0	0,0	0	<0,05	-0,60	0,0	0,0	0	<0,05	-0,61	0,0	0,0	0	<0,05
06.09.2007		-0,63	0,0	0,0	0	<0,05	-0,59	0,0	0,0	0	<0,05	-0,67	0,0	0,0	0	<0,05
07.09.2007	J _{ac} =30 A/m2	-0,66	0,0	3,5	30	<0,05	-0,59	0,0	0,6	30	<0,05	-0,67	0,0	0,6	30	<0,05
10.09.2007	J _{ac} = 100 A <i>l</i> m2	-0,68	0,0	11,5	100	<0,05	-0,61	0,0	2,0	100	<0,05	-0,69	0,0	2,0	100	<0,05
11.09.2007	J _{ac} = 200 A/m2	-0,72	0,0	23,1	200	<0,05	-0,65	0,0	4,0	200	<0,05	-0,73	0,0	4,0	200	<0,05
14.09.2007	J _{ac} = 500 A/m2	-0,76	0,0	57,7	500	<0,05	-0,69	0,0	10,0	500	<0,05	-0,77	0,0	9,9	500	<0,05
17.09.2007	J _{ac} =J _{dc} =0															
18.09.2007	U _{ein} =-1,27V	-1,28	-0,6	0,0	0	<0,05	-1,26	-1,3	0,0	0	<0,05	-1,28	-2,9	0,0	0	<0,05
19.09.2008		-1,28	-0,6	0,0	U	<0,05	1,26	-1,2	0,0	U	<0,05	-1,29	-3,1	0,0	U	<0,05
20.09.2008		1.27	-U,Б	0,0		<0.05	1.27	-1,1	0,0	U	<0.05	1.27	-2,0	0,0		<0,05
21.09.2007		4 27	-0,0	0,0	 	-0.05	4.07	-1,1	0,0		~0.05	4 27	-1,0 	0,0	 34	~0.05
21.09.2007	$U_{ac} = 0.5V$	1.07	-0,5	0,5	 	<0,05	1.27	-1,0	0,5	20 //2	<0,05	1.27	-2,0	0,5		<0,05
24.03.2007	U _{ac} = 0,05∛	-1.27	-0,5	2.0	15	<0,05 <0.05	1.1.27	-1.6	2.0	43 88	<0,05 <0.05	-1.27	-50	2.0	49	<u><0,05</u> ∠0.05
28.09.2007		-1 27	-0.8	30	26	<0.05	-1 27	-1.7	3.0	150	<0.05	-1.27	-10.0	3.0	205	0.37
08.10.2007		-1.27	-0.8	3.0	26	<0.05	-1,27	-1.5	3,0	150	<0.05	-1.27	-12.0	3.0	230	0,37
08 10 2007		-1 27	-10	60	57	<0.05	-1 27	-4.9	60	320		-1 27	-25.0	6.0	516	5.00
09.10.2007		-1.27	-1.0	6.0	58	<0.05	-1.27	-6.1	6.0	360	1.05	-1.27	-24.0	6.0	550	5.00
12.10.2007		-1,27	-1,1	6,0	61	<0,05	-1,27	-6,2	6,0	400	1,05	-1,27	-20,0	6,0	520	5,00
12 10 2007		-1 27	-11	7.0	61	<0.05	-1 17	-3.9	64	393	0.72	-1.02	-43	5.5	520	0.10
15.10.2007		-1,27	-1.1	7,0	61	<0.05	-1,27	-4,4	6,8	346	0,72	-1,12	-4.2	7.0	316	0,10
15 10 2007		-1 27	-1.5	151	133	0.05	-1 07	-3.3	14.6	780	0.45	-1 02	-43	15.0	735	<0.05
18.10.2007		-1.17	-1.8	14.9	143	0.05	-1.12	-3.6	15.0	715	0.45	-1.11	-2.1	17.4	470	<0.05
18 10 2007		_1 27	-22	14.9	143	0.05	-1.07	-27	15.0	715	0.24	_1 11	-21	17.4	470	
31 10 2007		-1 21	-20	14.7	140	0.05	-1.20	-11.0	13.5	775	1.00	-1.10	-12	18.1	335	<0.05
31 10 2007	II =₋1 64V	-1 64	-5.0	14.8	143	0.27	-0.98	-1.0	13.8	795	<0.05	1 11.0	-,- er	nd of te	et.	
05.11.2007		-1.60	-6.0	14.0	169	0.27	-1.03	-0.4	17.3	492	<0.05					
05 11 2007		_1 47	_4 7	14.8	180	0.27		end of test			-					
08.11.2007		-1.51	-5.2	14.5	180	0.27										
08 11 2007		_1 37	-39	14.5	180	0.27						-				
09.11.2007		-1.46	-5.0	14.4	180	0.27										
09 11 2007		_1 34	-39	14.4	180	0.27						-				
12 11 2007		-1 40	-4.3	14.1	178	0.27										
12 11 2007	II – 1.27V	1 27	20	14.1	178	0.06										
14 11 2007	0 on 1,27 V	-1.27	-32	14.2	175	0.06										
14 11 2007		1 17	2.2	14.2	175	0.05						-				
22 11 2007	0 _{en} ==1,17 V	-1.22	-2,2	14.2	168	0.05										
22.11.2007		4 4 2	1.0	444	100	-0.05						-				
22.11.2007	U ₀₀ =-1,12V	-1.15	-1.8	14.9	168	~0.05										
20.11.2001	LL = 1.07\/	4.07	4.4	444	460	-0.05						-				
26.11.2007	0 _{en} 1,07 V	-1.08		14,4	103	<0.05 <0.05										
20.11.2001	11 - 0.071/	0.07	0.4	447	150	~0.05						-				
20.11.2007	U _{an} =-0,97 V	-0,97	-0,4	14,7	130	<0,05 <0.05										
05 40 0007		0,35	-0,3	45.2	444	-0.05										
07.12.2007	U = U _R	-0.73	-0.4	15,5	144	<0,05									1	
07.40.0007		0.40		45.0	4.40	-0.05		Tat	ole 1	1.						_
10 12 2007	U = U _R	0.20	0,0	15,0	140	<0,05	Results from corresion									
10.12.2007	LL =0.4437	0.44	0.4	46.2	120	~0.05										
10.12.2007	U _{an} =0,11V	0,11	0,1	10,2	1/22	<0,05 20.05		l me	asu	reme	ents w	lith E	=R-st	eel	prope	s –
12.12.2007	11 0.0014	0,10	0,3 4 C	47.0	100	-0,05		in c	cem	entiti	ious n	nate	rials.	Pote	ential	- =
12.12.2007	U _{on} =0,38V	0,38	1,0	17,6	106	<0,05		values refer to Cu/CuSO₄-electrode.								
10.12.2007		0,33	0,0	10,0	03	4.00								2.00		
17.12.2007		0,89	4.0	10,5	00 10	1,20										
17 12 2007		0,34	1.0			1 00										
18 12 2007	Uac=0	0,90	1.0	0,0	μ	1,00										
10.12.2007		0,00	er	nd of te	est .											
		chu or test														

Fig. 7a, 7b and 7c show the results of these measurements. The corrosion rate (v_{corr}) is qualitatively shown as a function of the dc-current density (J_{dc}) and ac-current density (J_{ac}) and also as a function of on-potential (U_{on}) and ac-voltage (U_{ac}). Small circles/squares (filled or open) mean v_{corr} <0.05mm/a, medium size circles v_{corr} <0.5mm/a and large circles mean v_{corr} <0.5mm/a.

Results are summarized as follows.

Material I (fig. 7a, table 1):

- Corrosion rate at rest potential is negligible up to J_{ac}=500A/m² corresponding to U_{ac}=58V (see squares)
- At U_{on}=-1.27V corrosion rate is negligible up to J_{ac}=170A/m² corresponding to U_{ac}=15V (see open circles). It should be noted that J_{dc} becomes more cathodic with increasing J_{ac}, which should be due to a faradic rectification effect.
- Further shift to more negative on-potential (-1.64V) under unmodified U_{ac} and J_{ac} yields increasing corrosion rate (v_{corr}=0.27mm/a). Shifting the on-potential to more positive values again gives negligible corrosion rate (see filled circles).
- Under light anodic polarization corrosion rate is negligible but approximately follows the Faraday law at $U_{on}=1V$ probably due to acidification at the ER-probe interface (correction by the ohmic drop, however, yields $U_{IR-free} \approx 0.6V$ which is much too positive to expect active dissolution of steel).
- From the operational point of view the "safety range" under simultaneous cathodic protection and high voltage interference is U_{on} > -1.3V and U_{ac} < 15V (see dotted line in fig. 7a (bottom)).



Fig. 7a Results from corrosion measurements with steel ERprobe in material I Material II (fig. 7b, table 1):

- Corrosion rate at rest potential is negligible up to J_{ac} =500A/m² corresponding to U_{ac} =10V (see squares).
- At U_{on}=-1.27V corrosion rate is negligible up to J_{ac}=150A/m² corresponding to U_{ac}=3V (see open circles). Increasing U_{ac} to 6V (J_{ac}=340A/m²) yields v_{corr}=1mm/a accompanied by J_{dc} becoming much more cathodic (under U_{on}=const.).
- Shifting the potential to U_{on}=-1V yields negligible corrosion rate (see filled circles).
- From the operational point of view the "safety range" under simultaneous cathodic protection and high voltage interference is $U_{on} > -1,3V$ and $U_{ac} < 4V$ (see dotted line in fig. 7b (bottom)).

Material III (fig. 7c, table 1):

- Corrosion rate at rest potential is negligible up to J_{ac}=500A/m² corresponding to U_{ac}=10V (see squares).
- At U_{on} =-1.27V corrosion rate becomes v_{corr} =0.37mm/a under J_{ac} =230A/m² corresponding to U_{ac} =3V (see open circles). J_{dc} strongly depends on J_{ac} (U_{on} =const.) again indicating a faradic rectification effect.
- Shifting the potential to U_{on}=-1.0V yields negligible corrosion rate (see filled circles).
- From the operational point of view the "safety range" under simultaneous cathodic protection and high voltage interference is $U_{on} > -1.3V$ and $U_{ac} < 3V$ (see dotted line in fig. 7c (bottom)).





Results from corrosion measurements with steel ER-probe in material III

Conclusion

Based on the results and from the corrosion protection point of view for the carrier pipe running through a casing that is to be filled with one of the three tested cementitious materials the following can be stated:

- No corrosion risk in either material has to be expected from the application of cathodic protection if interference from high voltage lines and/or electrified railways is negligible.
- No corrosion risk (at least over some days) in either material has to be expected if the carrier pipe is interfered by high voltage lines and/or electrified railways and cathodic protection is not applied.
- Under simultaneous load of cathodic protection and interference due to high voltage lines and/or electrified railways it is recommended to use material I. Preferentially due to its relatively high resistivity this material provides an appropriate range – and safety margin - for the adjustment of the cathodic protection on-potential and for the reduction of the ac-voltage on the pipeline.

Literature

[1] M. Büchler, C.-H. Voûte und H.-G. Schöneich; Evaluation of the effect of cathodic protection levels on the a.c. corrosion on pipelines; Proceedings EUROCOR-Congress 2007, Freiburg, Germany