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Abstract

This report presents the results from a study of the possibilities of using red mud, a waste product derived from the digestion of bauxite with a versatile mineralogical composition, as additive in concrete, grout mortar and cement paste. Two types of red mud from China were used in the experiments. Concrete in which 0–30% of the mass of the binder was replaced by red mud were cast for investigating the effect of red mud addition on the compressive strength and dry shrinkage of concrete. Grout mortars in which 0–30% of the mass of the binder was replaced by red mud were cast for investigating the effect of red mud addition on the flexural and compressive strengths, dry shrinkage and water permeability of mortar. Cement paste in which 0–30% of the mass of the binder was replaced by red mud were cast for investigating the effect of red mud addition on the capacity of Cs adsorption and ionic leaching. The results show that addition of red mud does not contribute to nor impair the strength of the concrete or grout mortar but instead acts as inert filler. The decrease in compressive strength of concrete with addition of red mud is mainly due to the increased water-cement ratio. There is no significant increase in dry shrinkage of concrete with addition of red mud, but there is a certain increase in dry shrinkage of grout mortar, especially when more than 20% of the binder is replaced by red mud. Addition of red mud in grout mortar significantly increases the water permeability of the mortar due to the increased water-cement ratio. Owing to the fluctuant results from the adsorption test, it is difficult to draw a conclusion of the adsorption capacity for Cs by addition of red mud in concrete. However, the preliminary results from a quick adsorption test indicated a good adsorption behavior of cement with the addition of red mud, especially at a low initial Cs concentration.

Sammanfattning

I denna rapport presenteras resultaten från en studie av möjligheterna att använda så kallat rött slam (eng. red mud), en restprodukt från anrikning av bauxit med en komplex mineralogisk sammansättning, som tillsats i betong, gjutningsbruk och cementpasta. Två typer av rött slam från Kina användes i experimenten och fokus låg på studier av hur egenskaperna hos de olika materialen påverkades när olika mängder av bindemedlet ersattes med rött slam. Följande studier genomfördes:

- För betong studerades hur tryckhållfasthet och uttorkningskrympning påverkades när 0–30 vikts-% av bindemedlet ersattes med rött slam.
- För gjutningsbruk studerades hur böjnings- och tryckhållfasthet, uttorkningskrympning samt vattenpermeabilitet påverkades när 0–30 vikts-% av bindemedlet ersattes med rött slam.
- För cementpasta studerades hur Cs-adsorptionskapacitet och urlakning av joner påverkades när 0–30 vikts-% av bindemedlet ersattes med rött slam.

Resultaten visade att hållfastheten hos betong eller gjutningsbruk varken förbättras eller försämras vid tillsats av rött slam i någon utsträckning utöver det som kan förklaras av det ökade vattencementtalet. Uttorkningskrympningen påverkas inte signifikant hos betong vid tillsats av rött slam. Däremot uppvisar gjutningsbruk en ökad uttorkningskrympning vid tillsats av rött slam och då särskilt när mer än 20 vikts-% av bindemedlet ersätts med rött slam. För gjutningsbruk noterades även att vattenpermeabiliteten ökade vid tillsats av rött slam, något som kan förklaras av det ökade vattencementtalet. På grund av de oregelbundna resultaten från adsorptionsstudierna är det svårt att dra några slutsatser rörande hur adsorptionskapaciteten för Cs påverkas vid tillsats av rött slam till betong. Dock indikerade de preliminära resultaten från en snabb adsorptionstest ett gott adsorptionsbeteende hos cement vid tillsats av rött slam, särskilt vid en låg initial Cs-koncentration.

Contents

1 Introduction

1.1 Background

Cementitious materials are common construction materials in repositories for nuclear waste. Typically concrete is used in the engineered barriers whereas grout is used to stabilise the waste in the waste containers but also to fill the voids between the waste packages. The main objective of this is to restrict or reduce the release of radionuclides from the repository by means of eliminating advective flow of water through the waste containers and barriers and to provide a material with a high sorption capacity for the radionuclides. In Figure 1-1 an image of the rock vault for intermediate-level waste, 1BMA, in the repository for short-lived radioactive waste, SFR, is shown. As shown in this image concrete is used in the barrier system surrounding the waste but upon closure also the voids between the waste containers inside the different compartments are planned to be filled with grout.

Recently interest has been focused on increasing the sorption capacity in the engineered barriers by adding other types of materials with a high sorption capacity for elements which sorb poorly on the cement paste to the engineered barriers in the repository (Krall 2012). In that report so-called red mud, a waste product from the digestion of bauxite, was identified as a material with beneficial properties to be used as additive to concrete and grout used in the repository.

Red mud is – as mentioned above – a waste product from the treatment of aluminium ore. The composition of red mud varies depending on the composition of the original ore, but the main constituents are oxides of different metals of which iron oxide, which gives the material its characteristic colour, is the most prevalent. Currently, no suitable use for red mud has been identified and for that reason it is stored in large dams adjacent to the treatment plants.

Although different ways to utilise red mud have been discussed in the literature (Kurdowski and Sorrentino 1996), this is still mainly considered to be industrial waste at the lowest rate of use. In the past decades, limited studies were made to investigate the adsorption of Cs-137 and Sr-90 onto red mud (Apak et al. 1995). As Krall (2012) reviewed, the study by Apak et al. (1995) concluded that red muds may be utilised for constructing natural barriers around low-level radioactive wastes.

Figure 1-1. *Rock vault for intermediate-level waste, 1BMA, in SFR.*

1.2 Purpose and scope of this report

The purpose of the work presented in this report was to investigate the effects of using red mud as an additive in concrete and grout used in the engineered barriers in a repository for nuclear waste. Of particular interest is the use in a repository for long-lived low and intermediate level waste. The investigation work includes the following parts:

- Part 1: Investigating the effect of replacing a part of the cement binder with red mud in concrete on the hardened properties such as strength and shrinkage.
- Part 2: Investigating the effect of replacing a part of the cement binder with red mud in grout on the fresh properties, such as fluidity and stability, and the hardened properties, such as strength, shrinkage and water permeability.
- Part 3: Investigating the effect of replacing a part of the cement binder with red mud in cement paste on the alkali-leaching and adsorption of cesium ions.

2 Experimental

Specimens of concrete, grout and paste were prepared by mixing cement, water, ballast and red mud in different proportions according to Tables 2-3 to 2-8.

2.1 Raw materials

Two types of red mud were used in the experiments: Type 1 was taken from Chiping Xinfa Hoayu Alumina Co. LTD, Liaocheng City, Shandong Province, China and Type 2 taken from Xianfeng Alumina Co. LTD, Chongqing, China. The chemical compositions of red mud are listed in Table 2-1, where Type 1 was analysed by XRF (X-ray fluorescence) and Type 2 by EDPA volumetric titration according to Chinese standard GB 176-2008. It is noted that the loss of ignition (LOI) of red mud Type 2 is high and also that the calcium oxide content in red mud Type 2 is relatively high. According to the results from TGA (thermogravimetric analysis) as shown in Figure 2-1, the mass loss for calcite at 750–800°C (Gabrovšek et al. 2006) is not significant. This means that the calcium in red mud Type 2 is in the form of CaO, which may contribute to the hydration products, as will be discussed later.

Portland cement, P.II 52.5 from Shandong Cement Works Co., Ltd., China, was used. The chemical composition of the cement is listed in Table 2-2. Local sands and stones were used as aggregate in concrete and grout.

Table 2-1. Chemical composition of red mud used in the study (% by weight)

	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	LOI*
Type 1	16.9	3.04	26.8	36.26	11.5	0.19	5.15	–
Type 2	13.13	20.48	26.48	8.04	3.68	0.74	3.65	18.24

* Loss of ignition: the mass reduction at the elevated temperature from 105°C to 950°C.

Table 2-2. Chemical composition of the cement (% by weight)

	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SO_2	MgO
P.II 525	20.9	63.12	5.02	3.12	0.3	0.76	3.72	3.27

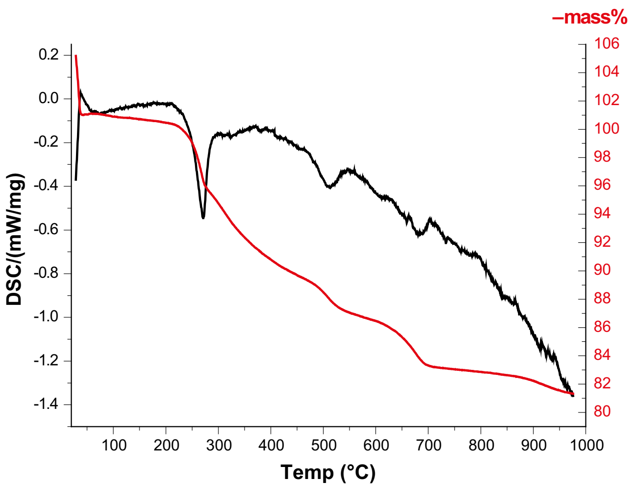

Figure 2-1. *Curve of mass loss of red mud Type 2 from Thermogravimetric analysis.*

2.2 Concrete

In order to keep the similar powder content in concrete mixtures, the addition of red mud was basically by replacement of cement, taking both cement and red mud as binder. In Shenzhen University, the binder was defined as the sum of cement and red mud by mass, whilst in Chongqing University the binder was defined as the sum of cement and 50% red mud by mass, based on their individual trials for the fresh concrete with desired workability.

Concrete with red mud by 0–30% mass of binder was manufactured to investigate the effect of red mud addition on the properties of concrete. The mix proportions and fresh property of concrete with red mud Type 1 and Type 2 are listed in Tables 2-3 and 2-4, respectively.

The concrete series CSZ was mixed in Shenzhen University using forced type mixer with 20 liters per batch whilst the concrete series CCQ was mixed in Chongqing University using forced type mixer with 24 liters per batch. 9 cubes of size 100 mm per each concrete mix were cast for compressive strength test and 3 prisms of size 100×100×400 mm per each concrete mix were cast for shrinkage test. Concrete specimens were cast, cured and tested according to Chinese national standards GB/T50080-2002, GB/T50081-2002 and GB/T50082-2009.

Table 2-3. Mix proportions of concrete with red mud Type 1

No.	Cement kg/m^3	Red mud kg/m^3	Sand/Stone kg/m^3	Water kg/m^3	w/b*	w/c	Slump (mm)
CSZ1-0	425	0	692/1,083	200	0.47	0.47	90
CSZ1-10	382.5	42.5	692/1,083	200	0.47	0.52	90
CSZ1-20	340	85	692/1,083	200	0.47	0.59	65
CSZ1-30	297.5	127.5	692/1,083	200	0.47	0.67	50
CSZ2-0	360	0	810/1,032	198	0.55	0.55	85
CSZ2-10	324	36	810/1,032	198	0.55	0.61	80
CSZ2-20	288	72	810/1,032	198	0.55	0.69	85
CSZ2-30	252	108	810/1,032	198	0.55	0.79	50
CSZ3-0	320	0	847/995	198.4	0.62	0.62	95
CSZ3-10	288	32	847/995	198.4	0.62	0.69	85
CSZ3-20	256	64	847/995	198.4	0.62	0.78	60
CSZ3-30	224	96	847/995	198.4	0.62	0.89	50

* w/b is water-binder ratio with binder b = mass of cement + mass of red mud; w/c is water-cement ratio.

Table 2-4. Mix proportions of concrete with red mud Type 2

No.	Cement kg/m^3	Red mud kg/m^3	Sand/Stone kg/m^3	Water kg/m^3	w/b*	w/c	Slump (mm)
CCQ1-0	415	0	644/1,146	195	0.47	0.47	65
CCQ1-10	394	41.5	644/1,146	195	0.47	0.49	25
CCQ1-20	373.5	83	644/1,146	195	0.47	0.52	15
CCQ1-30	353	83	644/1,146	195	0.47	0.55	8
CCQ2-0	325	0	680/1,210	185	0.57	0.57	40
CCQ2-10	309	32.5	680/1,210	185	0.57	0.60	17
CCQ2-20	292.5	65	680/1,210	185	0.57	0.63	15
CCQ2-30	276	97.5	680/1,210	185	0.57	0.67	9

* w/b is water-binder ratio with binder b = mass of cement + 0.5×(mass of red mud); w/c is water-cement ratio.

2.3 Grout

Grouts with red mud by 0–30% mass of binder were manufactured for investigating the effect of red mud addition on the properties of mortar. The ratio of binder (cement + red mud) to sand was fixed at 1:3. The water-binder ratio was adjusted between 0.66 and 0.88 based on the fulfillment of the requirements in fluidity and stability specified in the Swedish industrial method VU-SC:16 (Vattenfall 1993) (flow time 20–45 seconds for 6 liters of grout) and the European standard SS-EN 445:2007 (segregation <2.5%), respectively. The detailed procedures of the fluidity test (adopted from VU-SC:16) and the stability test (adopted from SS-EN 445:2007) are given in Appendix A. The actual mix proportions and fresh properties of the grout with red mud Type 1 and Type 2 are listed in Tables 2-5 and 2-6, respectively.

The grout series MSZ was mixed in Shenzhen University with mortar mixer whilst the series MCQ was mixed in Chongqing University with mortar mixer. 9 prisms of size 40×40×160 mm per each grout mix were cast for flexural and compressive strength tests and 3 prisms of size 40×40×160 mm with studs per each grout mix were cast for shrinkage test. Six conic specimens of size Ø70×Ø80×30 mm (Figure 2-2) per each grout mix were cast for water permeability test (Figure 2-3) according to Chinese standard JGJ/T70-2009.

Table 2-5. Actual mix proportions of grout with red mud Type 1 (per batch)

No.	Cement (kg)	Red mud Type 1 (kg)	Sand (kg)	Water (kg)	w/b*(w/c)	Fluidity (sec)	Stability (%)
MSZ-0	5.14	0	15.82	4.11	0.80 (0.80)	23	1.4
MSZ-10	4.63	0.51	15.82	4.01	0.78 (0.87)	34	0.64
MSZ-20	4.11	1.03	15.82	4.11	0.80 (1.00)	25	1.07
MSZ-30	3.60	1.54	15.82	4.52	0.88 (1.26)	35	1.05

* w/b is water-binder ratio with binder b = mass of cement + mass of red mud; w/c is water-cement ratio.

Table 2-6. Actual mix proportions of grout with red mud Type 2 (per batch)

No.	Cement (kg)	Red mud Type 2 (kg)	Sand (kg)	Water (kg)	w/b*(w/c)	Fluidity (sec)	Stability (%)
MCQ-0	4.500	0	13.50	3.340	0.74 (0.74)	21	1.57
MCQ-10	4.275	0.45	13.50	3.334	0.71 (0.78)	25	1.48
MCQ-20	4.050	0.90	13.50	3.439	0.69 (0.85)	20	1.54
MCQ-30	3.825	1.35	13.50	3.418	0.66 (0.89)	30	1.72

* w/b is water-binder ratio with binder b = mass of cement + 0.5×(mass of red mud); w/c is water-cement ratio.

Figure 2-2. *Conic specimens for the water permeability test.*

Figure 2-3. *Apparatus for the water permeability test.*

2.4 Paste

Cement paste with red mud by 0–30% mass of binder were cast for investigating the effect of red mud addition on the capacity of Cs adsorption and ionic leaching. The actual mix proportions and fluidity of the paste with red mud Type 1 and Type 2 are listed in Tables 2-7 and 2-8, respectively.

The cement paste series PSZ was manufactured and tested in Shenzhen University whilst the series PCQ was manufactured and tested in Chongqing University. Deionized water was used as mixing water. The fresh paste was cast in plastic bottles of volume 330–500 ml with caps for sealed curing. After curing for more than 28 days the plastic bottles were removed and the hardened paste was crushed and ground under the moist conditions (in the moist room with RH >90%) in order to prevent the particles from carbonation. The ground particles were sieved in the tap water using two sieves, with 0.25 mm and 1 mm spacing, so that about 100 g of particles of size 0.25–1 mm were obtained per each mix for the adsorption test. The detailed procedures of the adsorption test are given in Appendix B.

Table 2-7. Actual mix proportions of cement paste with red mud Type 1 (per batch)

No.	Cement (g)	Red mud Type 1 (g)	Water (g)	w/b* (w/c)	Fluidity (mm)
PSZ-0	1,000	0	500	0.50 (0.50)	22
PSZ-5	950	50	500	0.50 (0.53)	21.7
PSZ-10	900	100	510	0.51 (0.57)	20.5
PSZ-15	850	150	536	0.54 (0.63)	21.5
PSZ-20	800	200	550	0.55 (0.69)	20.5
PSZ-30	700	300	570	0.57 (0.81)	21.0

* w/b is water-binder ratio with binder b = mass of cement + mass of red mud; w/c is water-cement ratio.

2.5 Testing Methods

The following methods were used to study the properties of the fresh and the hardened materials:

- Concrete slump: Chinese standard GB/T 50080-2002 (Abrams cone test), similar to ISO 1920-2.
- Concrete compressive strength: Chinese standard GB/T 50081-2002, similar to ISO 1920-4.
- Concrete shrinkage: Chinese standard GB/T 50082-2009 (8.2 Contact method).

Table 2-8. Actual mix proportions of cement paste with red mud Type 2 (per batch)

No.	Cement (g)	Red mud Type 2 (g)	Water (g)	w/b* (w/c)	Fluidity (mm)
PCQ-0	800	0	400	0.50 (0.50)	165
PCQ-5	780	40	400	0.49 (0.51)	166
PCQ-10	760	80	400	0.48 (0.53)	161
PCQ-15	740	120	400	0.49 (0.54)	170
PCQ-20	720	160	400	0.49 (0.56)	165
PCQ-30	680	240	400	0.49 (0.59)	178

* w/b is water-binder ratio with binder b = mass of cement + 0.5×(mass of red mud); w/c is water-cement ratio.

- Grout fluidity: Swedish industrial method VU-SC:16 (see Appendix A).
- Grout stability: European standard SS-EN 445.
- Grout strength: Chinese standard GB/T17671, similar to ISO 679.
- Grout shrinkage and permeability: Chinese standard JGJ/T70-2009.
- Paste adsorption and leaching: see Appendix B.
- Ion concentrations: ICP-MS (Inductively coupled plasma mass spectrometry) and AAS (Atomic absorption spectroscopy).

3 Results and Discussions

3.1 Effect of red mud on the properties of concrete

3.1.1 Compressive strength of concrete

The results from the measurements of compressive strength for the different concrete specimens are summarized in Figures 3-1 to 3-5. It can be seen that the 28 days compressive strength in general decreased with addition of red mud, especially when red mud Type 1 was used. The reduction in the compressive strength was less pronounced when red mud of Type 2 was added than when Type 1 was used. This was particularly obvious during the early stages of the curing of the specimens when no reduction in compressive strength was observed for specimens with addition of red mud Type 2.

When expressing the compressive strength versus water-cement ratio, we can find a relatively good linear relationship, as shown in Figure 3-6, indicating that red mud may just function as inert filler and has no cementitious effect for contribution to the strength development.

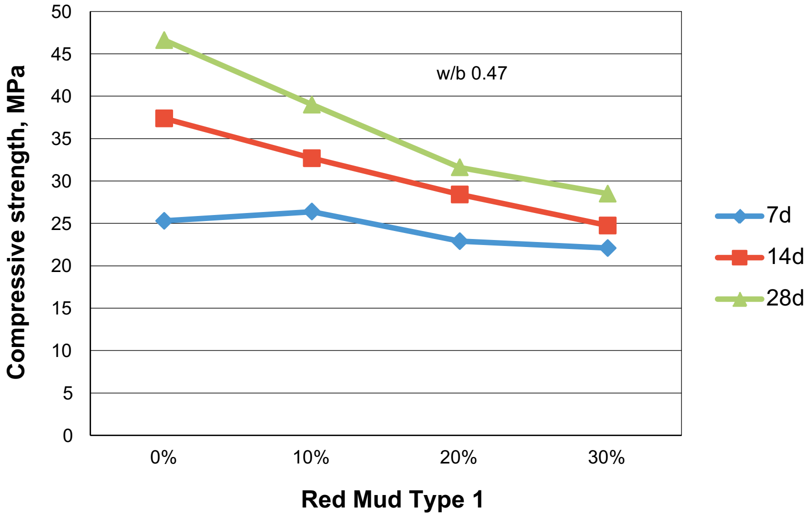

Figure 3-1. *Compressive strength of concrete with red mud of Type 1, w/b 0.47.*

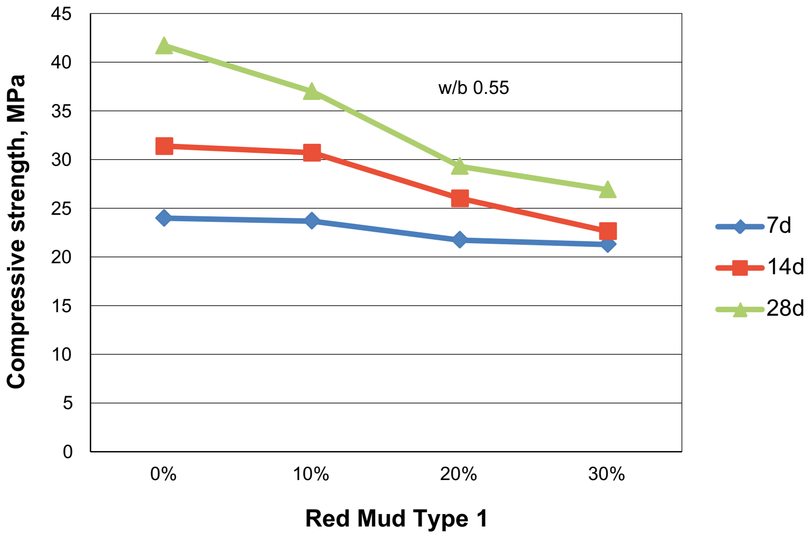

Figure 3-2. *Compressive strength of concrete with red mud of Type 1, w/b 0.55.*

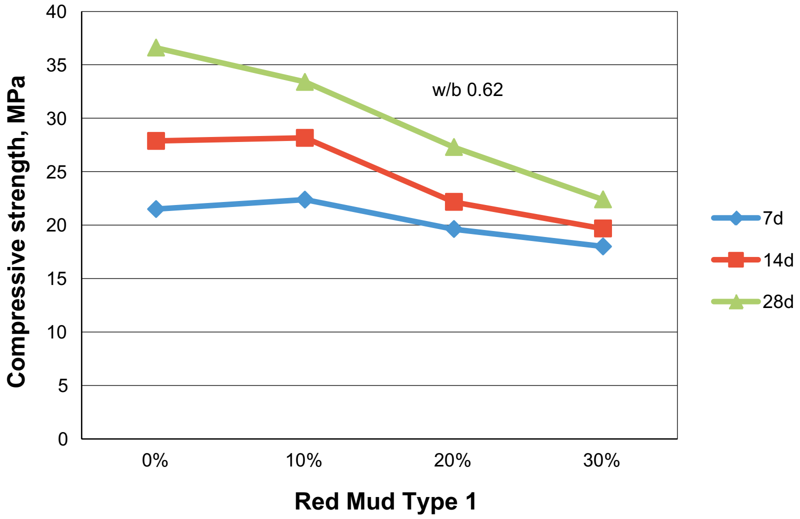

Figure 3-3. Compressive strength of concrete with red mud of Type 1, w/b 0.62.

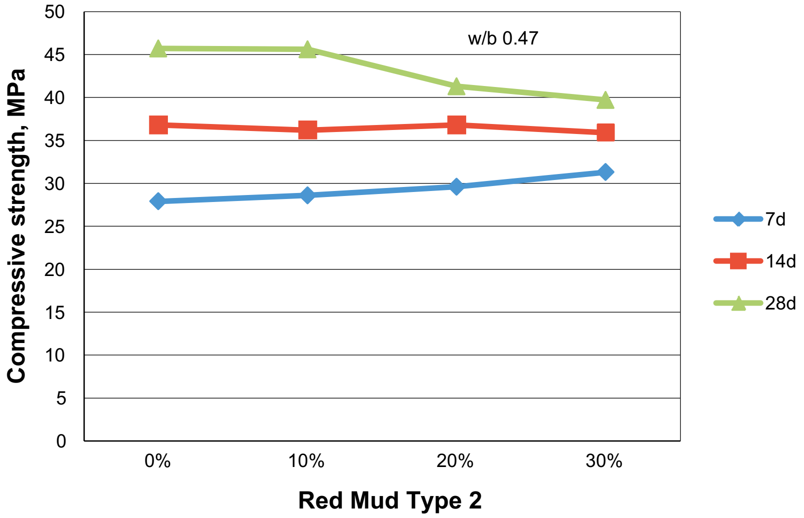

Figure 3-4. Compressive strength of concrete with red mud of Type 2, w/b 0.47.

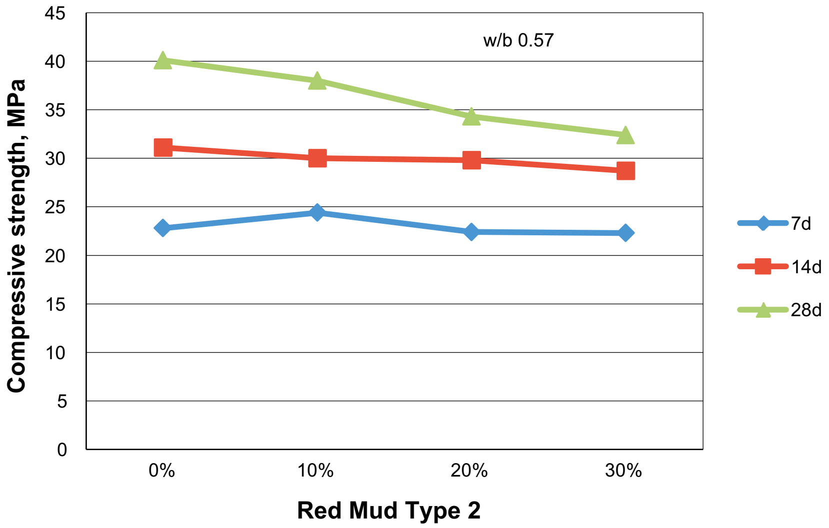

Figure 3-5. Compressive strength of concrete with red mud of Type 2, w/b 0.57.

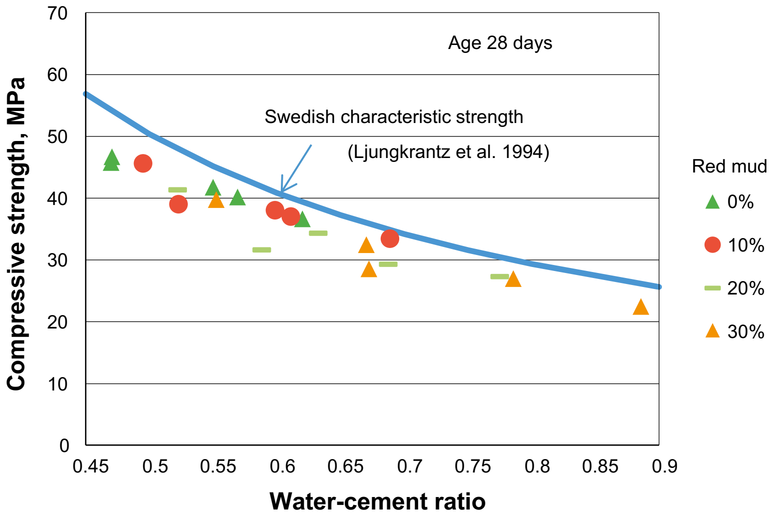

Figure 3-6. *Relationship between compressive strength and water-cement ratio of concrete containing different proportions of red mud Type 1 and Type 2. Swedish characteristic strength is based on Ljungkrantz et al. (1994).*

3.1.2 Shrinkage of concrete

According to Chinese standard GB/T 50082-2009, the concrete prisms shall be cured in the moist room at 20°C and RH >90% for 3 days before exposed to air at (20±2)°C and (65±5)% RH for shrinkage measurements. At Shenzhen University, due to the lack of personnel and the controlled climate room, the concrete prisms were cured in the water at 20°C for 14 days before exposed to air at 19°C and 56% RH for shrinkage measurements. The results of measured shrinkage of concrete with red mud of Type 1 are summarized in Figures 3-7 to 3-9. The results show that the dry shrinkage of concrete increased with the addition of red mud Type 1 and the shrinkage occurred mainly during the first day. The rapid shrinkage during the first day of exposure to air could be due to the loss of water in the coarse capillary pores which were saturated under the longer duration of water curing. Relatively high water-cement ratio in concrete with red mud Type 1 could be another reason to the increased dry shrinkage.

At Chongqing University, the concrete prisms were cured in the moist room at 20°C and RH >90% for 3 days before being exposed to air at about 20°C and 65% RH for shrinkage measurements, according to the standard procedure specified in Chinese standard GB/T 50082-2009. The results of measured shrinkage of concrete are summarized in Figures 3-10 to 3-11. The results show no significant difference in shrinkage between concretes with different amounts of addition of red mud Type 2.

Compared with the results presented in Figures 3-7 to 3-9, the shrinkages of concrete were more gradually increased, perhaps due to different initial degrees of water saturation, that is, a higher initial degree of water saturation in concrete with red mud Type 1 after water curing for 14 days than that in concrete with red mud Type 2 after moist curing for 3 days prior to the shrinkage measurement.

3.2 Effect of red mud on the properties of grout

3.2.1 Strength of grout

The results from measurements of flexural strength and compressive strength of grout are summarized in Figures 3-12 and 3-13. In these figures it is shown that the strength in general decreased with addition of red mud, especially when red mud of Type 1 was used. This confirms the findings presented in Figure 3-6 in which it is shown that the red mud functions as inert filler and does not contribute to the strength of the material. The decrease in strength is basically due to the increased water-cement ratio when part of the cement was substituted by the red mud. The reduction of strength was less pronounced when red mud of Type 2 was added compared to when red mud of type 1 was used. This can probably be explained by that the red mud of type 2 contains a smaller

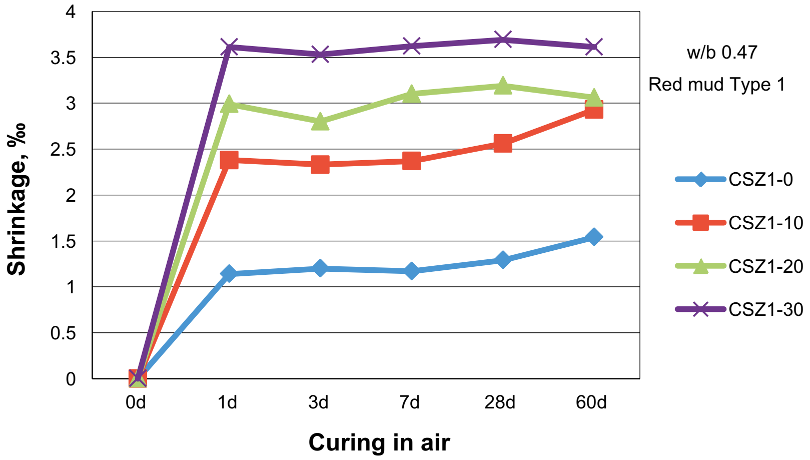

Figure 3-7. *Shrinkage of concrete with red mud Type 1, w/b 0.47.*

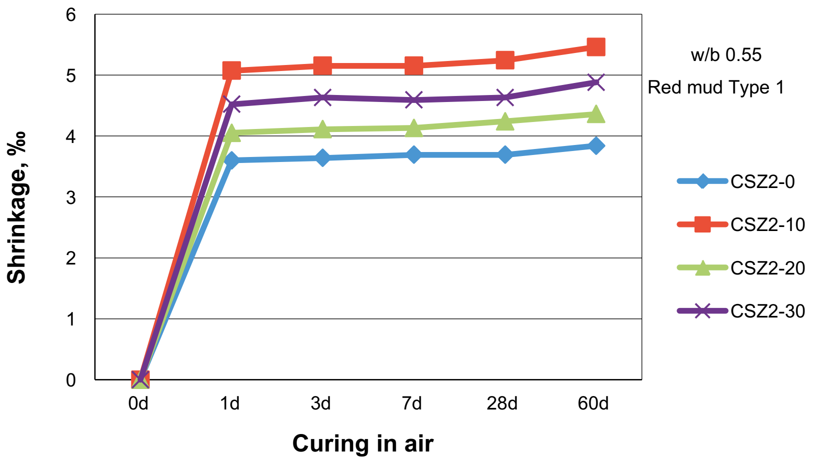

Figure 3-8. *Shrinkage of concrete with red mud Type 1, w/b 0.55.*

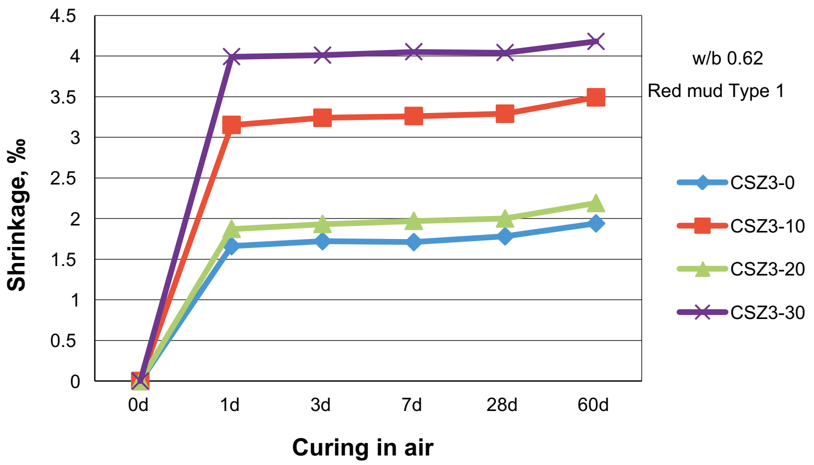

Figure 3-9. *Shrinkage of concrete with red mud Type 1, w/b 0.62.*

amount of ferric oxide but also that it contains a rather high amount of calcium oxide (as shown in Table 2-1), which can act as a binder in the material. As expected, both the flexural and compressive strengths of the grout with red mud Type 1 increased with increasing time for curing, owing to the continuation of hydration.

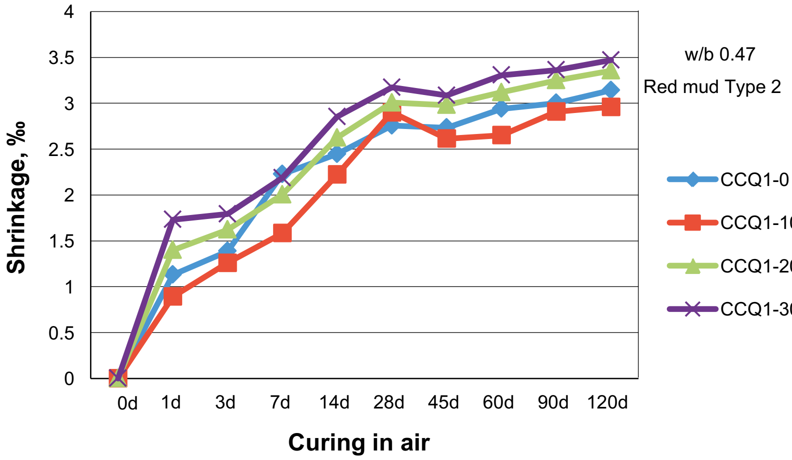

Figure 3-10. *Shrinkage of concrete with red mud Type 2, w/b 0.47.*

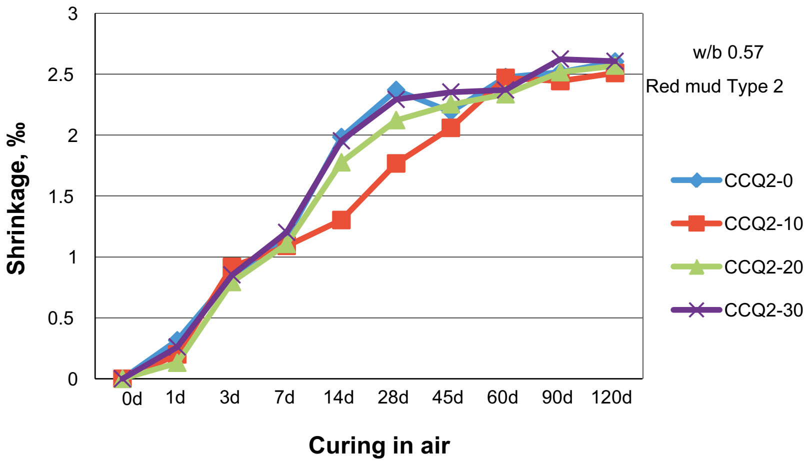

Figure 3-11. *Shrinkage of concrete with red mud Type 2, w/b 0.57.*

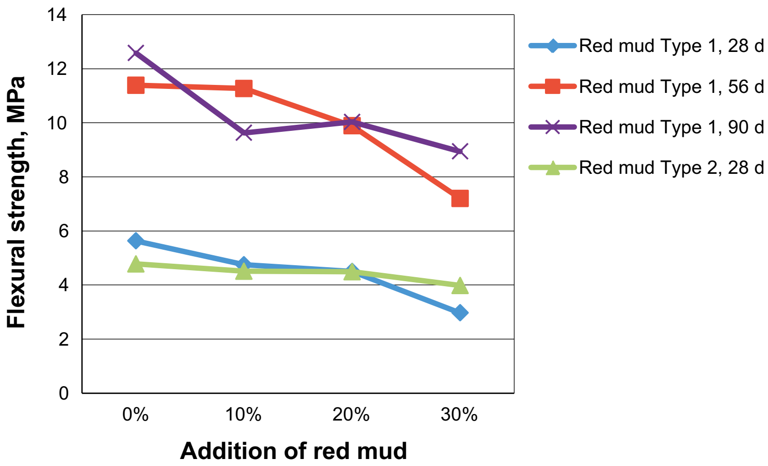

Figure 3-12. *Flexural strength of grout mortar with addition of red mud Types 1 and 2.*

3.2.2 Shrinkage of grout mortar

For the same reason as explained in Section 3.1.2, at Shenzhen University, the grout prisms were cured in water at 20°C for 42 days before being exposed to air at 19°C and 56% RH for shrinkage measurements. The results of measured shrinkage of grout are summarized in Figure 3-14. As in the case with concrete, shrinkage occurred mainly during the first day and no significant difference was

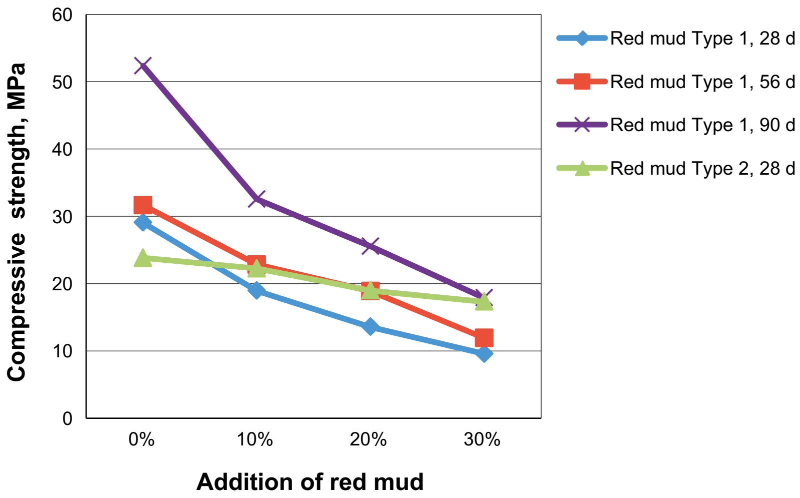

Figure 3-13. *Compressive strength of grout mortar with addition of red mud Types 1 and 2.*

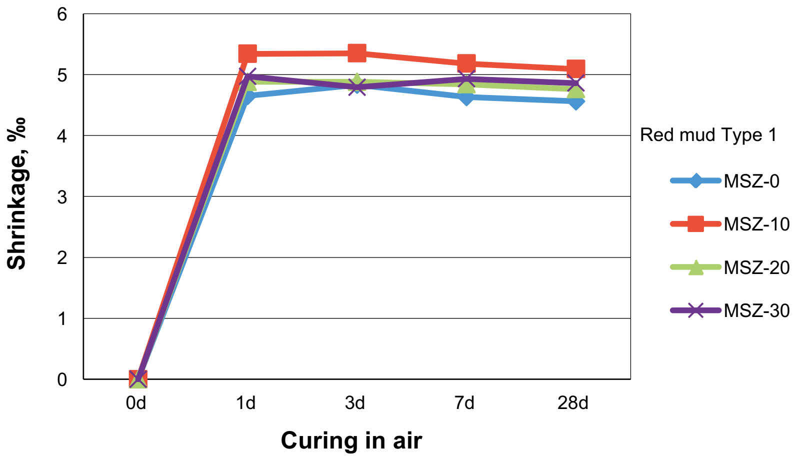

Figure 3-14. *Shrinkage of grout mortar with red mud Type 1.*

observed between the specimens with different amounts of red mud Type 1. This indicates that the long-term water curing caused swelling of the grout prisms and this swelling effect is larger than the effect of addition of red mud.

At Chongqing University, the grout prisms were cured in the moist room at 20°C and RH >90% for 7 days before exposed to the air at about 20°C and 65% RH for shrinkage measurements according to the standard procedure. The results of measured shrinkage of grout with red mud Type 2 are summarized in Figure 3-15, where a small increase in shrinkage of grout with Type 2 red mud can be observed. This should be reasonably expected, because the red mud functioned as inert filler and the shrinkage should just be the effects of cement content and water-cement ratio.

3.2.3 Water permeability of grout mortar

The water permeability was determined according to Chinese standard JGJ/T70-2009 (see Appendix C for a brief description of the test method), in which an initial pressure of 0.2 MPa with increment of 0.1 MPa per 2 hours is applied to the water on one side (Ø80 mm) of the conic specimen. When 3 of 6 specimens show penetrated water on the other side (Ø70 mm), the applied pressure is an indicator of water permeability. The results are summarized in Figure 3-16. It can be seen that the addition of red mud significantly decreased the penetrated water pressure of grout with red mud Type 1, tested at the age of 28 days, but not at the age of 56 days. The increased resistance of the grout with red mud to water pressure at 56 days may indicate reaction of red mud but a very slow reaction process. Further study is needed to investigate its long term effect. Regarding the water permeability of the grout with red mud Type 2, no significant trend can be seen from the test at the age of 28 days.

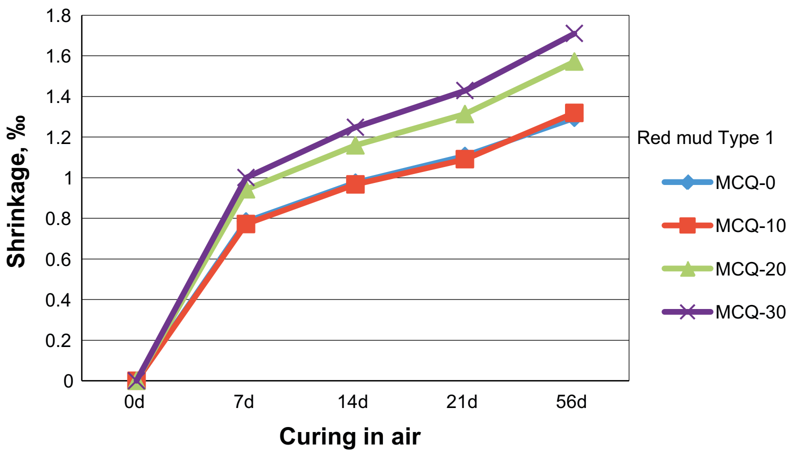

Figure 3-15. *Shrinkage of grout mortar with red mud Type 2.*

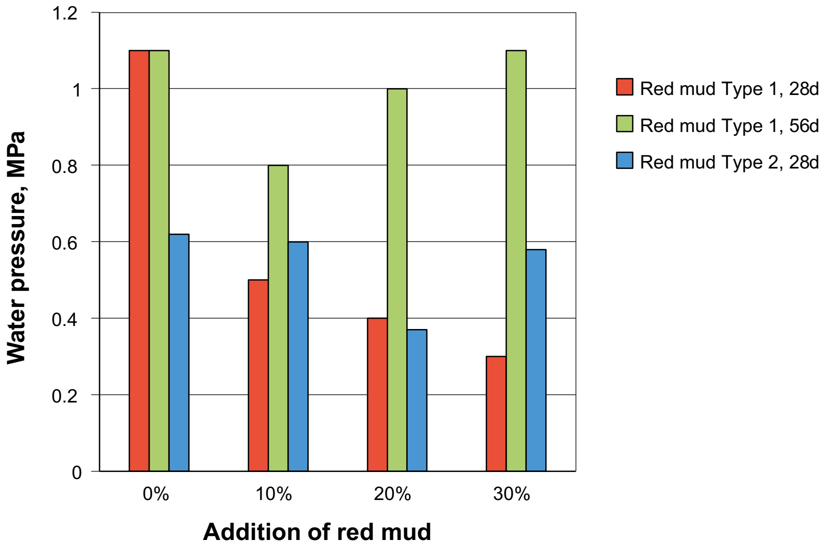

Figure 3-16. *Water permeability of grout with addition of red mud Type 1.*

3.3 Adsorption behavior

3.3.1 Cesium adsorption

Cesium ions are often used for simulating the adsorption behavior of cementitious materials to radionuclides due to its heavy molar weight and inactivity with cement hydrates. In the adsorption test 10 g homogenized dry particle sample of size 0.25–1 mm was immersed in 200 ml CsCl solutions with initial concentration of 0.3, 1, 3, 10, 30 and 100 ppm. After 3, 7 and 14 days the solution was sampled for chemical analysis using ICP-MS. The adsorption behavior should be seen from the reduction of Cs concentration in the solutions.

Figures 3-17 and 3-18 show the reduction of Cs concentration after 14 days immersion in the solutions with different initial concentrations of CsCl. No clear trend can be found from these results, indicating that the addition of red mud does not impair the adsorption behavior of cementitious materials.

However, the results show very fluctuant changes in Cs concentration, especially when the initial CsCl concentration is higher than 3 ppm. The measurement uncertainty could be one of the main reasons. To further investigate the adsorption behavior, a rapid adsorption test was carried out at Chalmers University of Technology, Section 3.3.2.

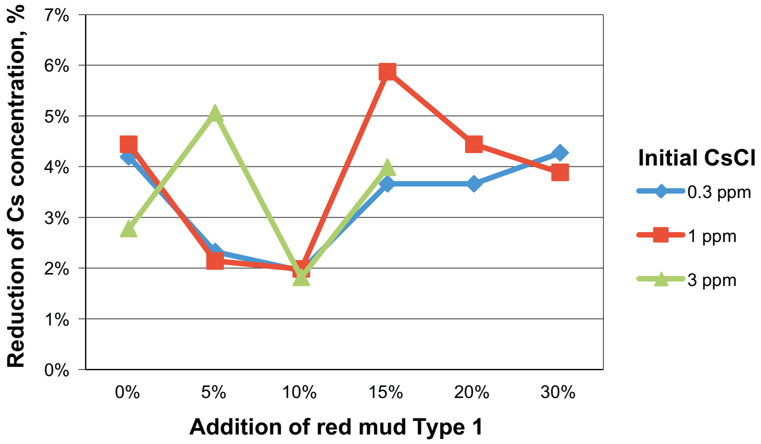

Figure 3-17. *Cs concentrations in the solutions after 14 days adsorption test of cement paste with addition of red mud Type 1.*

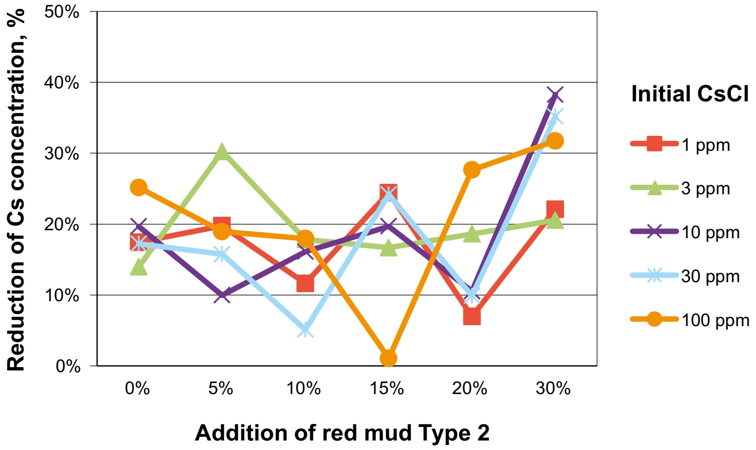

Figure 3-18. *Cs concentrations in the solutions after 14 days adsorption test of cement paste with addition of red mud Type 2.*

3.3.2 A quick adsorption test

In a conventional way the hardened cementitious samples are used for adsorption test. The time for hardening normally takes at least one month. In addition, during crushing and grinding it is difficult to prevent samples from carbonation, which may completely change the surface behavior of cementitious materials. Therefore, the conventional way is not only time-consuming but there are also uncertainties whether carbonation has been entirely avoided or not. This could be one of the reasons to the fluctuant results from the adsorption test as presented in Section 3.3.1. In order to make a quick evaluation of the adsorption properties under the carbonation-free condition we proposed a quick adsorption test. In this rapid adsorption test, Swedish cement for civil engineering (Anläggningscement) with different additions of red mud Type 1 (see Table 3-1) was mixed directly with CsCl solution in different initial concentrations (1–234 ppm) so that both long-term hardening and possible carbonation can be eliminated.

Table 3-1. Actual mix proportions of paste with red mud Type 1 for a quick adsorption test (per batch)

No.	Cement (g)	Red mud Type 1 (g)	Sand (g)	Solution* (g)
QAT-0	10	0	20	30
QAT-5	9.5	0.5	20	30
QAT-10	9	1	20	30
QAT-15	8.5	1.5	20	30
QAT-20	8	2	20	30
QAT-30	7	3	20	30

* CsCl solution in the initial concentration of 1–234 ppm.

Each mix was mixed in a 50 ml plastic test tube with a tight cap. The tube was hand-shaken for 1 minute and afterwards kept in a drum with rotation at 13–15 rpm for one week. The tubes were then placed still for 24 hours and the samples of 0.5 ml per each mix were taken from the bleeding liquid in each mix for Cs analysis by IC (Ion Chromatography). The results from this quick adsorption test are shown in Figure 3-19, in which the addition of red mud revealed an increased adsorption when the initial Cs concentration is lower than 23 ppm. It is worth pointing out that the remaining concentration of Cs is in general significantly lower than the initial concentration, indicating a good adsorption behavior of cement as well as with the addition of red mud.

3.3.3 Leaching of alkalis

Figures 3-20 and 3-21 show the concentrations of sodium (Na) and potassium (K) as well as calcium (Ca) in the 0.3 ppm CsCl solution after 14 days adsorption test of cement paste with addition of red mud. A trend is that the leached Na and K increased with the addition of red mud. This can be due to an increased water-cement ratio or permeability in the paste in combination with the high Na content in the red mud. This increased rate of Na and K leaching could be beneficial to Cs adsorption in the long-term, because the adsorption capacity of red mud increases with decreased alkalinity (Apak et al. 1995). The decreased Ca concentration in the paste with red mud Type 2 (Figure 3-21) could be due to the increase of Na and K ions in the solution which depressed the leaching of Ca from Portlandite.

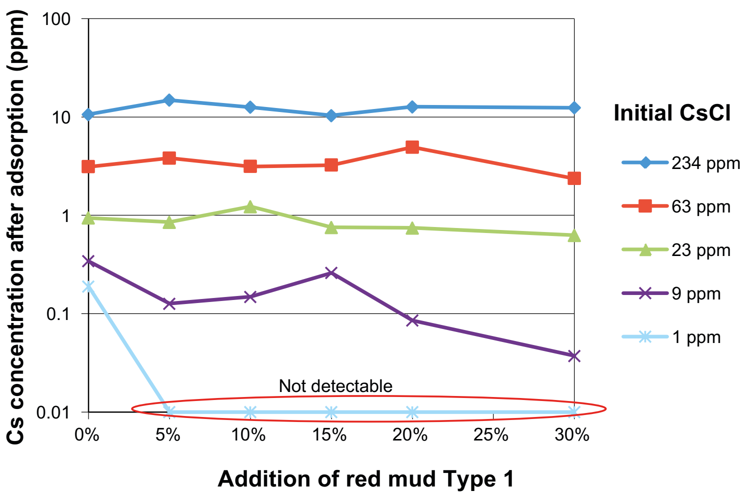

Figure 3-19. The cesium concentrations in the bleeding liquid after the quick adsorption test.

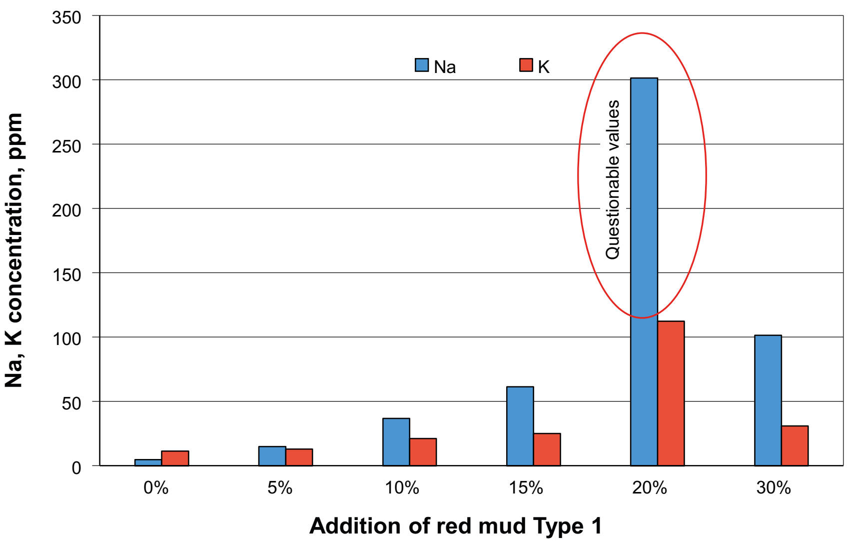

***Figure 3-20.** The sodium (Na) and potassium (K) concentrations in the 0.3 ppm CsCl solution after 14 days adsorption test of cement paste with addition of red mud Type 1.*

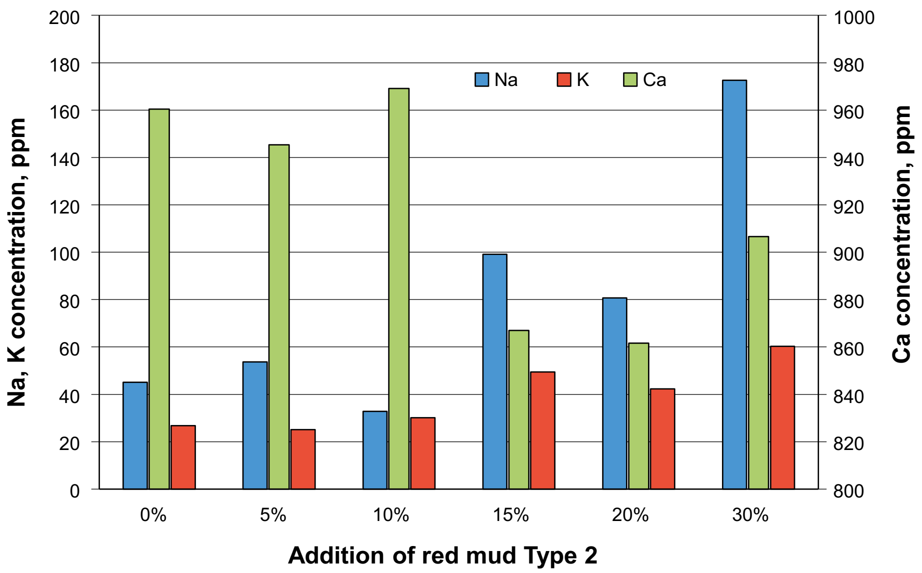

Figure 3-21. *The sodium and potassium as well as calcium concentrations in the 0.3 ppm CsCl solution after 14 days adsorption test of cement paste with addition of red mud Type 2.*

4 Summary and conclusions

This study reports on how the material properties are influenced by the addition of red mud to concrete, grout mortar and cement paste. It has been shown that:

- Red mud does not contribute to nor impair the strength of the concrete or grout mortar but instead acts as inert filler. The decrease in compressive strength of concrete with addition of red mud is mainly due to the increased water-cement ratio.
- There is no significant increase in dry shrinkage of concrete with addition of red mud, but there is a certain increase in dry shrinkage of grout mortar, especially when more than 20% of the binder is replaced by red mud.
- Addition of red mud in grout mortar significantly increases the water permeability of the mortar. This can also be explained by the increased water-cement ratio in the material, which led to the formation of more and larger capillary pores for water permeation.
- No clear trend of Cs adsorption is found from the adsorption test carried out in Chinese universities, probably due to the uncertainty of Cs-analysis used in this study and also due to the relatively high alkalinity in the pore solution.
- The Cs-adsorption at lower initial concentrations increases with the addition of red mud from the quick adsorption test carried out at Chalmers University of Technology, indicating a promising use of red mud in concrete for increasing immobilization of radionuclides.

Based on these results the following conclusions can be made:

- Red mud is not chemically active in the hydration process and the decrease in compressive strength of concrete with the addition of red mud is mainly due to the increased water-cement ratio.
- The increase in water permeability can be explained by that the water-cement ratio is increased when a portion of the cement is replaced by the inert red mud.

Owing to the fluctuant results from the adsorption test, it is difficult to draw a conclusion of the adsorption capacity for Cs by addition of red mud in concrete. However, the preliminary results from a quick adsorption test indicated a good adsorption behavior of cement with the addition of red mud, especially at a low initial Cs concentration (Figure 3-19). Because the adsorption behavior of red mud is strongly dependent on the alkalinity (Apak et al. 1995), in the future work the addition of red mud in concrete and grout with low alkalinity should be investigated. It may include:

- Addition of red mud in the concrete with high silica fume content. The alkali in the red mud can in the short term accelerate the hydration of silica fume and in the long term leach out to give more adsorption sites for radionuclides.
- Development of low alkali binders using e.g. slags activated with near neutral salts as immobilization binders for radionuclides.
- Adsorption test on the aged specimens with addition of red mud.

As a summary, red mud can be used in concrete and grout at least as a part of fine aggregate. The preliminary results show that its good adsorption behavior can potentially be utilized for immobilization of radionuclides in the nuclear wastes.

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Appendix A

Fluidity and stability tests

A1 Fluidity test for grout

The fluidity test is based on Swedish test method VU-SC:16, developed in 1993 by Vattenfall Development AB, currently Vattenfall Research and Development, VRD.

Equipment:

- Funnel made of stainless steel with a volume of about 7.5 liters and internal dimensions in mm as shown in Figure A-1.
- Holder of the funnel.
- Container with a volume of 10 liters with marking at 6 liters.
- Stopwatch.

Test procedure:

- The funnel is moistened and completely filled with grout while the bottom is sealed by hand.
- The stopwatch is started when the bottom of the funnel is opened.
- The time is measured when the grout flowed through the funnel to the container up to the 6 liters mark as well as when the light is visible through the bottom of the funnel.

The measured times are given in seconds without decimal.

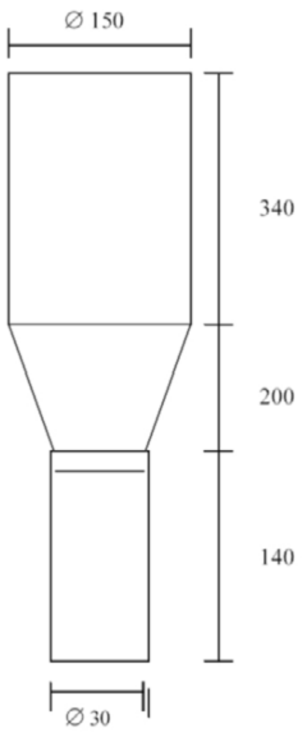

Figure A-1. *Schematic of funnel for the fluidity test (in mm)*

A2 Stability test for grout

The stability test is based on the relevant parts for water separation and setting in SS-EN 445:2007 Grout for prestressing tendons – Test methods.

Equipment:

- Test tubes, diameter about 50 mm and a volume of about 500 ml.
- Plastic film.
- Ruler.

Test procedure:

- Fill the grout into a test tube with a diameter of about 50 mm, height of about 200 mm so that the initial height of the grout is h0 (see Figure A-2).
- Use plastic film to seal the opening of the test tube, so that the sample is allowed to stand for 24 hours.
- Measure the height (h1) of the water column formed above the grout in the test tube to determine the degree of water separation.
- Measure the final height (h2) of the grout to determine the settlement.

Water separation is equal to the water column (h1) divided by the initial height (h0), expressed in percent, that is, h1/h0×100%, with one decimal.

The setting is equal to 1 minus the final height (h2) and divided by the initial height (h0), expressed in percent, that is, (1 – h2)/h0×100%, with one decimal.

Because temperature can affect water separation, all samples should be kept under constant temperature, +20 ± 2°C, for the results to be comparable.

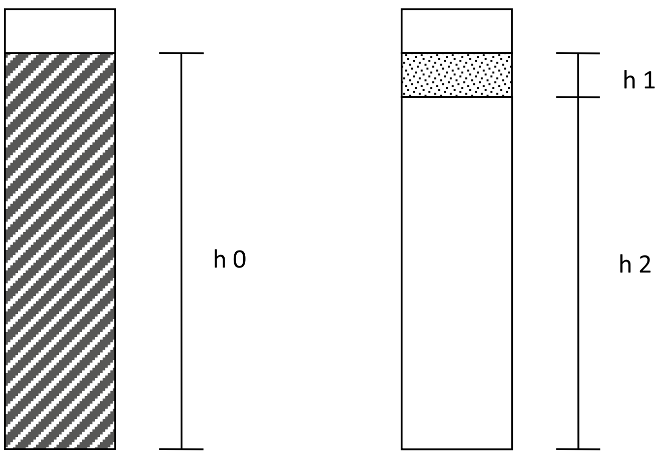

__Figure A-2.__ Schematic of the grout column for the stability test

Appendix B

Adsorption and leaching test

Proposed by Tang Luping

B1 Preparation of samples

- After casting, cure the paste specimens at ≥20°C under the sealed condition for at least 28 days.
- Crush the well-cured paste specimens using suitable tools under wet or moist condition (by spraying water) to small pieces.
- Wet-grind the small pieces by hand using a suitable grinding bowl (e.g. ceramic mortar) and using distilled water as wetting medium in order to prevent the samples from carbonation due to the CO_2 in the air.
- Sieve the ground particles in the tap water with two sieves, i.e. 0.25 mm and 1 mm; removing the particles with size <0.25 mm and re-crush the particles with size >1 mm by repeating the above procedure until more than 100 g of the particles with the sizes between 0.25 to 1 mm is obtained.
- Filter away the excess water from the particles using rapid filter paper.
- After filtering, immediately place the particle samples into a vacuum desiccator or vacuum dryer (such as DZF6050 or 6090) for vacuum drying under a vacuum condition (absolute pressure <200 mbar or a pressure <800 mbar relative to the atmospheric pressure) at a temperature of 55–60°C for 3–7 days. (Note: Vacuum is necessary for preventing samples from carbonation due to CO_2 in the air. If the temperature cannot be elevated, the drying period shall be prolonged to more than 2 weeks).
- After drying, keep the samples in a sealed container or desiccator with drying agents such as silicate gels for later use.

B2 Preparation of solutions

- Use anhydrous cesium chloride (CsCl) with a purity of 99.99% and distilled water to prepare CsCl solutions with the approximate concentrations of 100 mg/l (100 ppm); 30 mg/l (30 ppm); 10 mg/l (10 ppm); 3 mg/l (3 ppm); 1 mg/l (1 ppm); and 0.3 mg/l (0.3 ppm). (Note: for 6 types of samples you need to prepare about 2 L solution for each concentration)
- Store each solution in a polypropylene container (bottle or jerrican) with lid for tightness. (Note: Polypropylene container shall be used because glassware can adsorb Cs)

B3 Adsorption and leaching test

- Weigh 10 g homogenized dry particle sample and put it into a 250 ml polypropylene bottle.
- Fill the bottle with 200 ml (or 200 g) solution and then tight the bottle with lid.
- Store the bottle in a climate room at constant temperature (about 25°C).
- Shake the bottle every working day for 10–20 seconds.
- Take 10 ml with pipette and seal the sample in a polypropylene test tube after storage for 3 days; 7 days and 14 days. (Note: You have totally 36 samples. Shake the samples first and take the sample after standing the bottles still for 30–60 minutes).
- Mark the samples and store them in a safe place for subsequent chemical analysis.

B4 Chemical analysis

- One of the methods for chemical analysis such as IC (ion chromatography), ICP-MS (Inductively coupled plasma mass spectrometry), or AAS (Atomic absorption spectroscopy) can be used for analysis of Cs^+, Na^+, K^+, Ca^{2+} ions in the solutions.
- The Cs-adsorption capacity of the cement paste with red much can be estimated by comparing the difference between the initial and the final Cs-concentration in the solution.
- The leaching behavior of the cement paste with red mud can be estimated by comparing the difference between the initial and the final K^+, Na^+ or Ca^{2+} concentration in the solution.

Appendix C

Water permeability test

The water permeability test of grout is based on the relevant part for testing the resistance of building mortar to water permeability in Chinese standard JGJ/T70-2009: Standard for test method of performance on building mortar.

Equipment:

- Conic metallic molds with base plate for specimen casting, with upper diameter 70 mm, lower diameter 80 mm, height 30 mm.
- Mortar permeameter, a typical example is shown in Figure C-1.

Test procedure:

- The mold is filled with the mixed grout, stirred with a spatula several times. When the filled grout is slightly higher than the upper edge, the excess grout is scraped off with a spatula in a 45° angle off, and the grout surface is evened and finished using the spatula in a relatively flat angle. Six specimens per test series should be cast.
- After casting, specimens should be cured at room temperature (20 ± 5)°C for (24 ± 2) h before demolding. Afterwards the specimens are stored at temperature (20 ± 2)°C, humidity of >90% to the required curing age (28 and/or 56 days in this study). Prior to the permeability test, the specimens are moved to the laboratory room for the surface drying, and assembled onto the permeameter with sealing materials.
- An initial water pressure of 0.2 MPa is applied to the specimens and kept for 2 h before being increased to 0.3MPa. Afterwards the pressure is increased by 0.1 MPa per each hour until the water is permeated through three of six specimens. If the water leakage surrounding the curved surface occurred during the test, the test should be stopped and the specimens should be re-assembled with sealing materials.

The permeability index is calculated using the following equation:

$$P = H - 0.1$$

where P is the permeability index and H the pressure at which the water is permeated through three of six specimens.

Figure C-1. *Example of mortar permeameter for water permeability test.*