THE EFFECT OF HIGH SALT CONCENTRATION ON THE INTEGRITY OF SILICA-FUME BLENDED CEMENTITIOUS MATRICES FOR WASTE IMMOBILIZATION APPLICATIONS

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Abstract

Silica Fume is a commonly used pozzolanic additive for cementitious matrices used for waste immobilization purposes. During the last years several publications have shown that commercially available densified silica-fume (DSF) does not fully disperse within cementitious pastes and concrete mixes, but rather tends to form agglomerated particles which range in size from tens to hundreds of microns. Cementitious matrices containing such agglomerates are prone to the alkali-silica reaction (ASR). As radioactive waste streams often contain high alkali salt concentrations, the occurrence of ASR in cementitious waste matrices must be considered. The aim of this research was to study the effect of high salt content in DSF bearing pastes on the integrity of the immobilized waste form. The dependence of matrix integrity on both salt and silica fume concentration is presented.

Keywords: ASR, densified silica-fume, waste immobilization

1   INTRODUCTION

Waste streams usually contain complex mixtures of ionic species, often at high concentrations, only some of which are toxic or radioactive. While the immobilization matrix must bind and retain the toxic component, it must also be compatible with the remaining ionic components. In the case of radioactive waste immobilization using cementitious materials, high salt concentrations can interfere in the cement hydration process and even inhibit it [1]. In addition, the presence of diverse ionic species can change the equilibrium concentration of the different species in the paste and hence affect the immobilization mechanism.

Silica fume has been used for many years as a mineral additive for cement and was found to improve strength, durability and resistivity of cementitious products. It has been considered an appropriate additive to cementitious pastes used for waste immobilization applications due to its pozzolanic reactivity together with its absorbance capability. However, during the last years several publications have shown that in some cases, the commercial densified silica fume (DSF) product is not homogenously dispersed within cementitious matrices [2, 3]. Agglomerates sizing from 10's to 100's of microns persist within the matrix, despite the use of vigorous mechanical mixing, supersonic homogenization techniques or the addition of super-plasticizers. The presence of such agglomerates was mainly observed for cement pastes, although there are some reports of DSF agglomerates in concrete mixes and mortars as well. Agglomeration has significant consequences for mix performance, as it affects its water consumption and reduces the extent of the pozzolanic reaction as well as the space-filling effect, all of the above leading to reduced mechanical properties. In addition, Diamond [3, 4] has shown that these silica-fume agglomerates are prone to the alkali-silica reaction (ASR) rather than suppress it, as it was common to believe.

While the mechanism of the ASR is still not completely clear, most researchers believe that the combination of large siliceous particles together with high Alkali ion concentration within the pore solution are the two main factors leading to the destructive reaction. The deterioration of cementitious matrices is due to swelling of the gel formed by the reaction of the alkali-containing pore solution with reactive silica in the aggregates. The swelling of the gel generates tensile stresses within the specimen, resulting in expansion and cracking.

Previous studies of Cesium (Cs) ion immobilization in DSF blended cementitious pastes show that the presence of the silica fume agglomerates greatly improves the immobilization of Cs ions by a

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combined mechanism of adsorption to the unreacted silica left at the agglomerate core, together with the formation of a hydration rim around the silica particles, which serves as an additional diffusion barrier for the immobilized ions and thus further improves its immobilization [5].

The aim of the present study is to test the effect of high $NaNO_3$ concentrations, representing the main component in typical radioactive waste streams, on the integrity of DSF blended cementitious waste forms - containing agglomerated silica-fume particles, and thus potentially susceptible to the alkali silica reaction.

2   MATERIALS AND METHODS

2.1   Materials and mix designs

Ordinary Portland cement (OPC) CEM I 52.5N, conforming to EN 197, obtained from Nesher, Israel, was used throughout this work, blended with either densified silica-fume (DSF) or raw silica-fume (RSF), both from Scancem Chemicals, Norway. Table 1 presents the mineral composition of the different materials used as given by the manufacturers. All pastes were prepared at constant water to binder (w/b) ratio of 0.45.

Salt bearing matrices used in the leaching experiments were prepared by dissolving appropriate amounts of sodium nitrate ($NaNO_3$, Aldrich chemicals), representing the main ionic species in the waste stream, and cesium nitrate ($CsNO_3$ Aldrich chemicals), representing the radioelement to be immobilized, in the mix water, to yield a total Na content of 1.4 mmol/g paste, and a Cs content of 0.02 mmol/g paste. The cementitious pastes were blended with either 10 wt% DSF, 20 wt% DSF or 20 wt% raw silica fume (RSF). An unblended OPC paste served as a reference. Table 2 presents the composition of the pastes used for the leaching experiments.

Samples for the ASR immersion test were prepared by adding varying amount of sodium salts, either sodium nitrate ($NaNO_3$, Aldrich chemicals) or sodium chloride (NaCl, Aldrich chemicals) to the mix water, yielding final Na ion concentrations of 0.4, 0.6, 0.8, 1.2, 1.7 mmol/g paste. DSF replaced cement at 10 wt% and 20 wt% loadings. Table 3 presents the composition of the pastes used for the immersion experiments.

The dry components and solutions were mixed in a 5-liter Hobart mixer and cast in plastic molds (diameter 40 mm, height 100 mm), sealed and rotated for the first 24 hours to prevent bleeding and segregation. As the ions were added during paste preparation, it was assumed that the ions were evenly dispersed and had sufficient time to interact with the paste; i.e. to become chemically bound or incorporated by other effects. After setting, the samples were removed from the molds, inserted into polypropylene bags, sealed again in order to prevent exposure to the atmosphere, and allowed to self-cure at room temperature for 28 days.

After curing, matrices prepared for the leaching experiments were cut using a 35mm diamond blade (water cooled), into 15-mm thick discs. ASR immersion tests were carried out with the cured cylinders without further processing.

2.2   Methods for assessment and analysis

Scanning Electron microscopy analysis (SEM)

SEM analysis (Secondary electron image at 20KV), together with EDS using standard less ZAF correction, was employed to characterize both the local morphology and chemical composition of the different paste samples (Quanta 200, FEI SEM, SEM-EDAX laboratory, Ben-Gurion University). Specimens prepared for SEM analysis were fractured and oven-dried at 105^0C for 2 hours. The dried fractured face was gold-coated for analysis.

Immersion experiments

Unlike the usual immersion test, where the cementitious sample is immersed in a salt solution and the dimensions of the sample are monitored during the test, in this case study the salts were an integral part of the cement paste, and the ingress of water into the sample was the trigger of their degradation process.

Cylindrical samples (diameter 40 mm, height 100 mm) were immersed in deionised water, and their integrity was monitored during the first hours following immersion and on a daily basis thereafter. Photographs of the samples were taken at various times.

Leaching experiments

Leaching tests were performed according to the ANSI/ANS-16.1 (1986) procedure [6], using deionized water as the leachant. The leaching tests were performed using duplicate samples of the pastes. Analysis of the leached Cs ions was performed using inductively coupled plasma – mass

spectrometry (ICP-MS) (VG PlasmaQuadIII, Environmental Analytical Laboratory, Ben-Gurion University), LLD for Cs <2 ppb.

3 RESULTS

DSF blended cementitious pastes containing 1.4 mmol sodium nitrate/g paste and 0.02 mmol Cs ions/g paste (introduced as CsNO3) were subjected to leaching experiments in order to study the effect of high alkali ion concentrations on the immobilization of Cs ions. The results of these experiments, expressed as the cumulative fraction of Cs ions extracted as a function of time, are presented in Figure 1. Each curve represents the average leaching value of duplicate samples.

The paste blended with 10 wt% DSF preformed better than an unblended paste, with only 0.55 of the total Cs leaching during a 3 month period, and did not show any sign of degradation. The 20% DSF blended paste, on the other hand, performed very poorly. The samples started to crack within minutes after submersion in water, with cracks growing larger and significant swelling taking place leading to disintegration of the sample within several days (See Figure 2.). The gradual disintegration of the cementitious paste resulted in the increased release of Cs ion from the matrix. The cumulative fraction of Cesium ions released from the sample reached a value of 0.6 within 7 days, and the experiment was discontinued at this stage. The relatively large error bars corresponding to the experimental curve of this sample originate from the random nature of the cracking process which affects the leaching results. A SEM image of a fracture surface within this sample is presented in Figure 3. The cracks in the sample developed along the DSF agglomerates, which seem to have been damaged by the reaction. The small spherical particles found within the cracks were analyzed using EDS and identified as $NaNO_3$, implying that high salt concentrations were present at the cracking sites and might have been involved in the process.

The detrimental role of the DSF agglomerates in the cracking process is verified by comparing this result with that obtained for samples blended with 20 wt% raw SF. These samples remained intact throughout the 3 months immersion in water, releasing only 0.27 of the total Cs during this period.

In order to obtain a quantitative estimate of the alkali and DSF content which give rise to ASR, a series of cementitious pastes containing varying salt concentrations and blended with either 10 wt% or 20 wt% DSF has been prepared. Sodium ions were introduced into these samples as either the nitrate or chloride salt. Figure 4 presents photographs of these samples after 14 days of immersion in water. The samples prepared with 10 wt% DSF did not show any significant degradation during this period. Few minor cracks were detected in samples containing $NaNO_3$ at Na ion concentrations of 1.2 mmol Na / g paste or higher, yet with no evident swelling. In contrast, pastes blended with 20 wt% DSF containing $NaNO_3$ showed significant cracking for salt concentrations above 0.6 mmol / g sample. In this group of samples cracking appeared within 1h of immersion and was accompanied by significant swelling of the samples and extruded gel, both typical to the ASR reaction.

Pastes blended with 20 wt% DSF and containing NaCl exhibited a much more moderate reaction and developed less cracking. Gel- like droplets were observed on the surface of these samples but no swelling has occurred.

4 DISCUSSION

The very high leaching values obtained for the Cs ions represent a well-known problem in radioactive waste immobilization. Cs ions are difficult to immobilize due to their large size and high solubility [7, 8]. In a previous publication we have shown that the addition of DSF to the paste greatly reduces the leachability of the Cs ion [5]. We had proposed that the lower Cs leachability is due to a combination of two mechanisms, adsorption of the Cs ions by the unreacted silica within the DSF agglomerates, and the creation of a reaction rim around the DSF agglomerate. This reaction rim serves as an additional diffusion barrier for the Cs ions, thus increasing the efficiency of Cs immobilization (a reduction of two orders of magnitude in the apparent diffusion coefficient)..The creation of such a rim has been reported in several publications [4,7,9]. Ichikawa and co-workers have recently proposed a modified mechanism of the ASR, involving a reaction rim generated around ASR-affected aggregates. According to their interpretation, this reaction rim acts as a semipermeable hard membrane allowing the penetration of alkaline solution but preventing the leakage of viscous alkali silicate formed by the ASR, and thus creating expansive pressures leading to cracking of the aggregate and the surrounding matrix [9].

The results of the leaching experiment presented here show that at high alkali ion loading, which is typical for radioactive waste streams, the positive effect of the DSF agglomerates on the Cs ion immobilization may vanish due to the ASR reaction.

The severe cracking and swelling of DSF blended matrices during immersion in water is clearly demonstrated by the photograph of the degraded sample (Figure 2). Figure 3 confirms that the reaction occurs around the DSF agglomerates where cracks are being formed and eventually interconnect.

Mature pastes prepared with raw silica fume (RSF) do not contain agglomerated particles [5]. Indeed, for 20 wt% RSF blended pastes, even when bearing very high salt concentrations (1.4 mmol Na/g paste), no evidence of the deleterious ASR reaction was found; i.e, the samples did not develop cracks during the 90 day leaching experiment, and immobilization of the Cs ion was substantially more efficient than obtained with the unblended paste, as shown from leaching results (Figure 1).

The amount of DSF blended in the paste has a major effect on the extent of the ASR. Minor cracking had been formed in pastes blended with 10 wt% DSF and bearing the highest $NaNO_3$ concentrations. In this case the reaction was moderate; i.e. cracking appeared several days after the immersion of the samples in water, and no swelling or disintegration of the sample have been observed. Leaching experiments results (Figure 1) further prove that even with the presence of high salt concentration, the 10 wt% DSF blended paste remains an efficient immobilization matrix. On the other hand, samples containing 20 wt% DSF showed severe cracking within minutes of their exposure to water, which was followed by swelling and complete disintegration. We believe that the higher density of DSF agglomerates (20 wt%) within the matrices is at the origin of this different behavior. At high DSF blending cracks are more probable to interconnect, leading to total failure of the sample, whereas at lower DSF concentration the damage seems to remains at a more local level.

The difference in the extent of the ASR between samples loaded with $NaNO_3$ and those loaded with NaCl suggests that both the cation and anion are involved in the ASR reaction. The role of the counter ion on the extent of the ASR reaction is not yet clear to us and it will be a topic for future research.

This preliminary study can give some guidelines as to mix design using the threshold salt concentrations obtained for each DSF loadings. Future research will focus on a more detailed understanding of the ASR reaction and the effects of additional parameters such as DSF particle size, water to cement ratio and the nature of the alkali ion, as well as the role of the salt counter ion in the reaction.

5   CONCLUSIONS

- High alkali salt concentrations, incorporated in DSF blended cementitious pastes (containing agglomerated silica-fume particles) induce the occurrence of the deleterious alkali silica reaction (ASR).
- The ASR appears upon immersion of the sample in water. Cracks rapidly appear, growing larger and eventually (within hours or days) significant swelling takes place leading to disintegration of the sample.
- SEM analysis reveals that the cracks run along the surface of the agglomerated DSF particles.
- The ASR was found to depend on the silica-fume loading, alkali salt concentration and the nature of the counter ion.
- The threshold salt concentrations obtained for each DSF loading in this preliminary study can serve as a basic guideline to mix design.

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TABLE 1: Mineral composition of the materials* (%wt).

	OPC	DSF	RSF
CaO	63.23	0.48	0.33
SiO_2	19.15	91.7	92.01
Al_2O_3	5.47	0.75	0.40
Fe_2O_3 total	2.89	2.33	0.91
MgO	1.32	0.85	1.25
TiO_2	0.40	na	na
K_2O	0.46	1.16	1.40
Na_2O	0.20	0.30	0.39
P_2O_5	0.51	na	na
Mn_2O_3	0.04	na	na
SO_3	2.97	0.25	0.33
Cl	0.01	0.07	0.13
LOI total	3.17	1.78	1.70
Sum total	99.82	99.67	98.85
Na_2O equivalent	0.50	1.06	1.31

* as given by the manufacturers

TABLE 2: Composition of pastes used in the leaching experiment (g)

Sample name	PC	water	DSF	RSF	$CsNO_3$	$NaNO_3$
No additives	500	225	-	-	3.125	100
DSF 10%	450	225	50	-	3.125	100
DSF 20%	400	225	100	-	3.125	100
RSF 20%	400	225	-	100	3.125	100

TABLE 3: Composition of pastes used in the immersion tests (g)

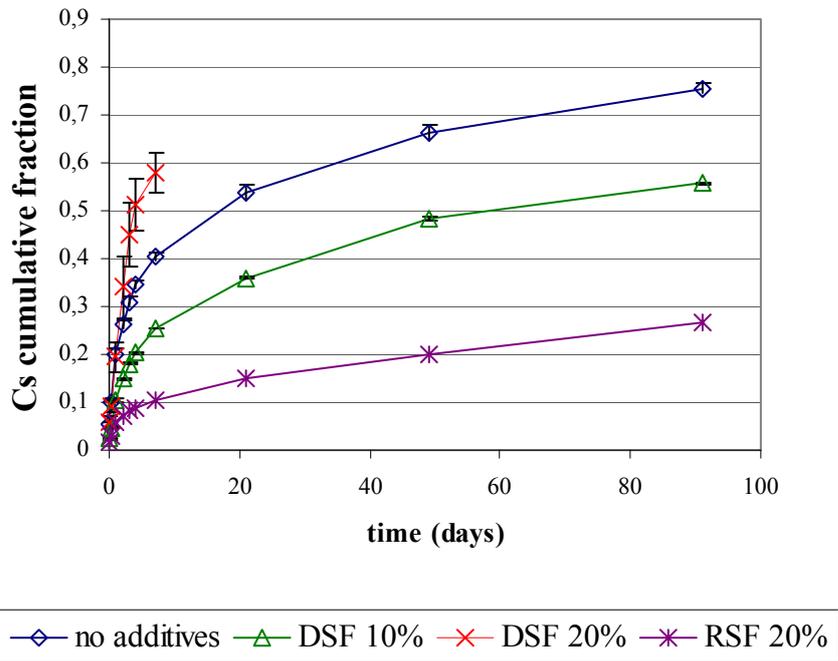| Sample name	PC	water	DSF	$NaNO_3$	NaCl	mmol Na /g paste
AS-11	450	225	50	26	-	0.41
AS-12	450	225	50	40	-	0.62
AS-13	450	225	50	55	-	0.83
AS-14	450	225	50	87	-	1.26
AS-15	450	225	50	123	-	1.71
AS-22	400	225	100	26	-	0.41
AS-16	400	225	100	40	-	0.62
AS-17	400	225	100	55	-	0.83
AS-26	400	225	100	87	-	1.26
AS-18	400	225	100	-	27	0.61
AS-19	400	225	100	-	36	0.82
AS-20	400	225	100	-	57	1.24
AS-21	400	225	100	-	79	1.68

Figure 1: Cumulative fraction of Cs ions as a function of time from leaching experiments using cementitious pastes with/without silica-fume. Samples were prepared at w/c=0.45 and contained high $NaNO_3$ concentration (1.4 mmol Na / g sample). DSF=densified silica-fume, RSF=raw silica-fume.

Figure 2: Photograph of a 20%wt DSF blended cementitious paste sample after a few days immersion in water during the leaching experiment.
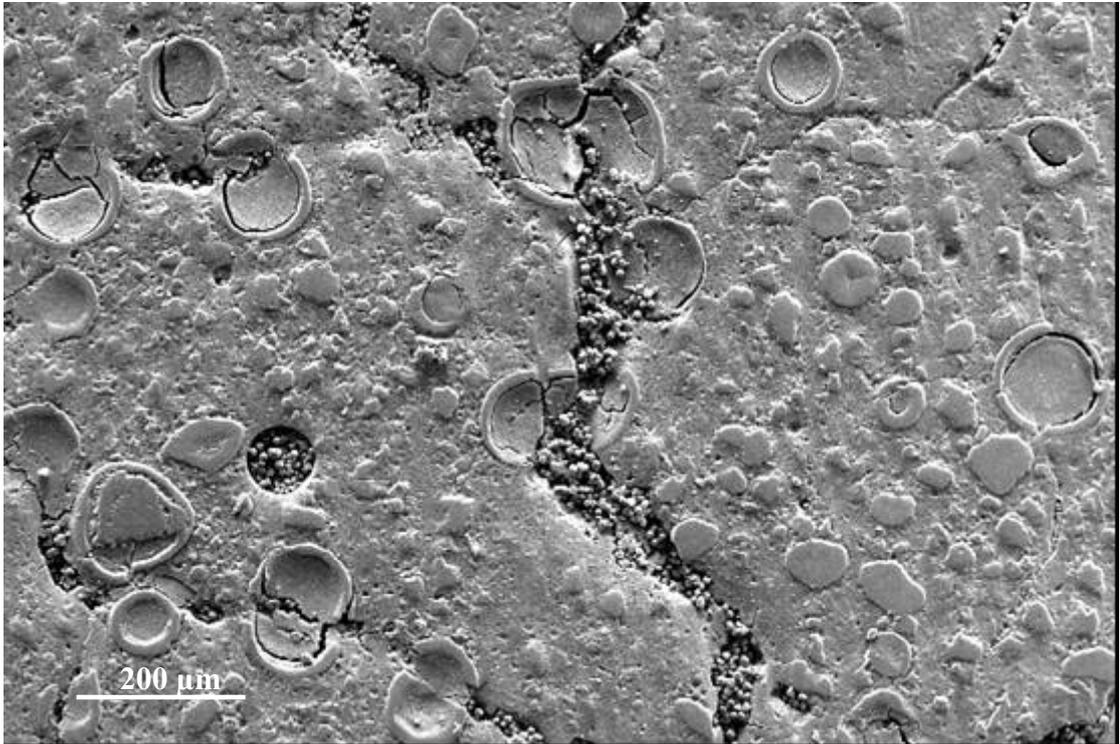
Figure 3: SEM image of a 20%wt DSF blended cementitious sample containing high $NaNO_3$ concentration after a few days immersion in water. Secondary electron scanning at 20KV.

	10%wt DSF, NaNO₃	20%wt DSF, NaNO₃	20%wt DSF, NaCl

10%wt DSF, NaNO$_3$ | **20%wt DSF, NaNO$_3$** | **20%wt DSF, NaCl**

0.4 mmol Na/g paste — AS11 דגם | AS22 דגם

0.6 mmol Na/g paste — AS12 דגם | AS16 דגם | AS18 דגם

0.8 mmol Na/g paste — AS13 דגם | AS17 דגם | AS19 דגם

1.2 mmol Na/g paste — AS14 דגם | | AS20 דגם

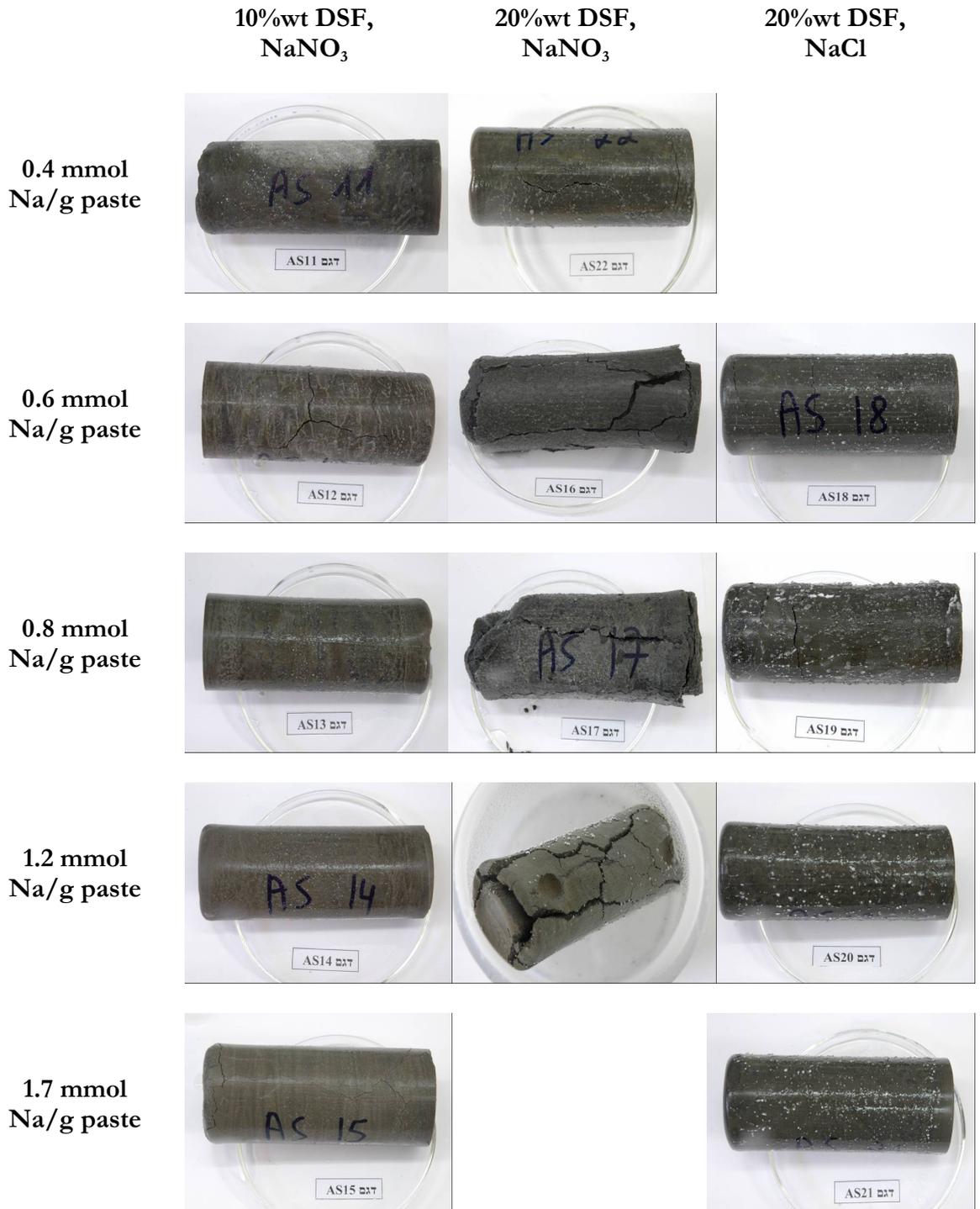**1.7 mmol Na/g paste** — AS15 דגם | | AS21 דגם

Figure 4: Photographs of the samples following the ASR immersion tests. The tested samples vary in their alkali salt concentration (0.4-1.7 mmol Na / g sample), the DSF blending (10%wt, 20%wt) and the nature of the anion (NO$_3^-$, Cl$^-$). Photographs were taken after a 14 days immersion period.