

# DURABILITY PERFORMANCE OF RFCC SPENT CATALYST-BLENDED PORTLAND CEMENT PASTE EXPOSED TO SEA WATER ATTACK

<sup>#</sup>ALI ALLAHVERDI, MEHDI MAHDAVAN

*Cement Research Center, School of Chemical Engineering,  
Iran University of Science and Technology, Narmak 16846-13114, Tehran, Iran*

<sup>#</sup>E-mail: ali.allahverdi@iust.ac.ir

Submitted May 13, 2013; accepted November 28, 2013

**Keywords:** Spent Catalyst, Catalytic cracking unit, Portland cement, Sea water

*This paper discusses the performance of the paste of Portland cement blended with spent catalyst from Resid Fluidized Catalytic Cracking (RFCC) unit of petroleum refining processes in sea water. 28-day cured paste specimens prepared from binary cement mixes containing different amounts of spent catalyst were exposed to Persian Gulf sea water. Compressive strength, weight, and length changes of the specimens were monitored and considered for evaluating the extent of deterioration. Laboratory techniques of X-ray diffractometry, scanning electron microscopy, and Energy dispersive X-ray spectroscopy were also used to study the deteriorated specimens. The results confirm that at relatively high replacement levels, the pozzolanic property of the spent catalyst and the increased open pore volume of such blended cements may result in contradictory consequences. Specimens of relatively higher replacement levels exhibit higher rates of deterioration in spite of their superior mechanical strength behavior caused by pozzolanic reaction. The results obtained by X-ray diffractometry confirm the presence of higher amounts of chlorine-containing Friedel's salt in specimens containing RFCC spent catalyst compared to plain reference specimens.*

## INTRODUCTION

Spent catalyst from RFCC units contaminated with some heavy metals should be disposed in a safe way. Recent studies have confirmed that this spent catalyst exhibits strong pozzolanic activity [1]. Utilization of this material as an additive in Portland cement is probably much better than land-filling, since it is reported that not only heavy metals are well immobilized, but also considerable improvements in mechanical properties of the cement are achieved [2-4]. Such improvements in mechanical properties of cement are due to pozzolanic reaction between spent catalyst and calcium hydroxide produced in the hydration of the Portland cement phases. Our research works, however, have revealed that incorporation of this industrial waste material into Portland cement can lead to increased open pore volume and water absorption of the hardened cements paste at early ages due to the highly porous microstructure of the catalyst particles [5]. Knowing the importance of the permeability of the cement-based materials as a durability determining factor in aggressive environments, detailed experimental works are necessary to investigate the effects of RFCC spent catalyst on durability of cement based-materials in aggressive environments. An important aggressive environment for Portland cements is sea water. Cement-based materials exposed to sea water can be subjected to various kinds of physical

and chemical attacks. The physical attack can take the form of freeze-thaw, salt weathering, and abrasion. The chemical attack is due mainly to chloride ingress and sulphate attack [6, 7]. Sea water typically contains sodium chloride, magnesium chloride, potassium bicarbonate, and perhaps most significantly magnesium sulphate and calcium sulphate. The mechanism of sea water attack on cement-based materials is very different than what is happening in the case of pure sulphate attack. Deterioration due to expansion has been shown to be of less importance in the case of sea water attack [7]. The pozzolanic property of RFCC spent catalyst has been claimed by many researchers, but the performance and durability of Portland cements blended with this industrial waste material in aggressive environments including sea water have not yet been investigated. The aim of this study is to evaluate the effects of RFCC spent catalyst on durability performance of hardened Portland cement paste in sea water.

## EXPERIMENTAL

### Materials and methods

The materials used in this study include Type II Portland cement in accordance with ASTM C150 (standard specification for Portland cement), and RFCC spent catalyst. According to ASTM C150, type two Portland

cement has a limited amount of calcium aluminate phase (< 8 wt.%) and therefore exhibits medium sulphate resistance. The RFCC spent catalyst was firstly ground in a laboratory ball mill for 100 minutes to obtain a relatively fine powder comparable to Portland cement. The particle size distribution of the catalyst powder was determined by a laser particle size analyzer and the values of specific surface area and bulk density of ground catalyst were measured in accordance with ASTM C204 (standard test methods for fineness of hydraulic cement by air-permeability apparatus) and ASTM C188-95 (standard test method for density of hydraulic cement), respectively.

The properties of both RFCC spent catalyst and Portland cement are shown in Table 1. The results of chemical analysis reveal that the catalyst is mainly made up of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. As seen, these two components account for over 95 % of the total weight of the material. This catalyst is therefore relatively high siliceous and according to ASTM C618 (standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete), it could chemically be considered as a relatively good artificial pozzolan.

Table 1. Properties of ground RFCC spent catalyst and Portland cement.

Chemical composition (wt. %)	Cement	Spent Catalyst
SiO <sub>2</sub>	20.26	58.43
Al <sub>2</sub> O <sub>3</sub>	5.43	37.32
Fe <sub>2</sub> O <sub>3</sub>	3.87	1.19
CaO	64.96	-
MgO	0.48	0.65
SO <sub>3</sub>	2.09	0.20
Na <sub>2</sub> O	0.27	0.82
K <sub>2</sub> O	0.60	0.11
TiO <sub>2</sub>	-	-
L.O.I	1.95	1.25
Free CaO	0.45	-
Bogue's phase composition (wt. %)	Cement	Spent Catalyst
C <sub>3</sub> S	54.54	-
C <sub>2</sub> S	17.01	-
C <sub>3</sub> A	7.84	-
C <sub>4</sub> AF	11.78	-
Physical properties	Cement	Spent Catalyst
Blaine Fineness (m <sup>2</sup> /kg)	320	315
Density (kg/m <sup>3</sup> )	3130	2470

Laser particle size analyzer (Sympatec, GmbH, HDD), X-ray diffractometry (JEOL JDX-8030), and Thermogravimetry (Netzsch model 429) were the principal laboratory techniques used in this study for material characterisation. Figure 1 shows the particle size distributions of spent catalyst before and after grinding, respectively. As seen, after grinding the weight fraction of particles less than 50 µm has been significantly increased

with almost 95 % of the grains in the range 5 - 90 µm that is comparable to the particle size distribution of Portland cement.

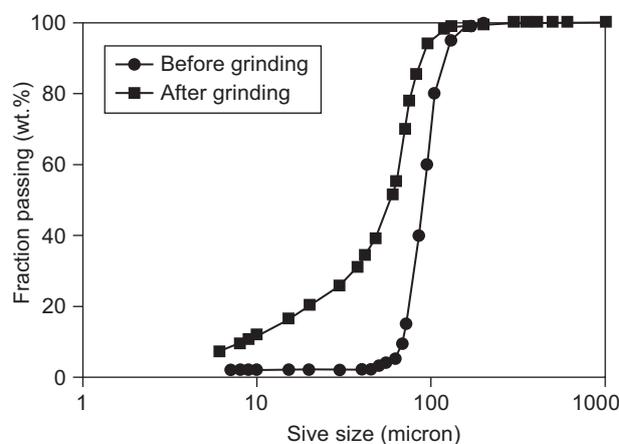


Figure 1. Particle size distribution of RFCC spent catalyst.

The mineralogical composition of the spent catalyst was determined by the use of powder X-ray diffractometry (Cu K $\alpha$  radiation). Figure 2 shows the X-ray diffraction pattern of the material. As seen, the shape of the pattern and the broad diffuse halo at 2 $\theta$ -angle of 23 degrees clearly shows that the spent catalyst is mainly an amorphous material. The few minor crystalline mineral phases present in the material are faujasite ((Na<sub>2</sub>,Ca,Mg)<sub>3.5</sub>[Al<sub>7</sub>Si<sub>17</sub>O<sub>48</sub>]·32(H<sub>2</sub>O)), quartz (SiO<sub>2</sub>), and kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>).

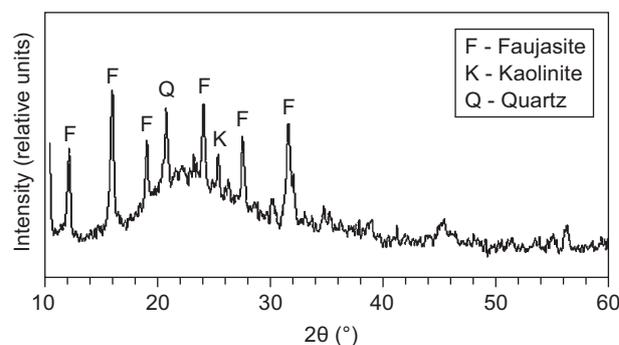


Figure 2. X-ray diffraction pattern of RFCC spent catalyst.

Pozzolanic activity of the spent catalyst was also investigated based on thermogravimetric analysis of cured lime-catalyst paste. A thoroughly homogenized binary mixture of calcium hydroxide and spent catalyst at equal proportions was utilized for preparing a paste at a water-to-dry material ratio of 1. The paste was then stored at an ambient of N<sub>2</sub> atmosphere at 60°C for being cured. After given time periods, the paste was firstly dried with acetone and N<sub>2</sub> gas and then utilized for measuring the amount of reacted calcium hydroxide by thermogravimetric analysis. The pozzolanic activity

of the spent catalyst was then compared to silica fume as the strongest pozzolanic material and also to different natural pozzolans being utilized by the Iranian cement industry. As seen in Table 2, RFCC spent catalyst can be considered as a relatively high quality artificial pozzolanic material compared to silica fume and natural pozzolans.

Table 2. Pozzolanic activity of RFCC spent catalyst compared to silica fume and some natural pozzolans.

Days	1	3	7	14	28
Material	Lime consumption (wt. % by weight of material)				
Silica fume	84.46	97.57	100	–	–
RFCC spent catalyst	–	66.82	–	69.14	70.28
Taftan natural pozzolan	–	42.26	58.75	60.36	64.87
Bojnord natural pozzolan	–	28.18	37.98	40.03	53.14
Sirjan natural pozzolan	–	33.39	38.45	42.58	48.72

#### Specimens Preparation

Binary cement mixes were prepared with 0, 10, 20, and 30 wt. % replacement of Portland cement with ground spent catalyst. Water-to-cement ratio was taken constant at 0.30 for all the mixes and fresh pastes were cast into cubic specimens of the size 20×20×20 mm. The expansion measurements were conducted on two 20×20×100 mm prismatic paste specimen. The moulds were stored at an atmosphere of more than 95 % relative humidity at 25°C for the first 24 hours and then the specimens were cured in tap water at 25°C for 27 days.

#### Test Procedure

After curing, the specimens were exposed to sea water directly taken from Persian Gulf. A sample of sea water was analyzed for its soluble salts or ions. The concentrations of sodium and potassium ions were determined by flame-photometry (Jenway PFP7). The laboratory technique of atomic absorption spectrophotometry (Techtron, A100) was applied for determining the magnesium and calcium ions concentrations. The concentrations of chlorine and sulphate ions were determined in accordance with ASTM D4458 (standard test method for chloride ions in brackish water, seawater, and brines) and ASTM D4130 (standard test method for sulfate ion in brackish water, seawater, and brines), respectively. The obtained results are presented in Table 3.

Table 3. Concentration of sea water ions.

Ion	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Concentration (ppm)	11 400	397	1 600	450	22 330	3 070

The sea water temperature was kept constant at 25°C throughout exposure time. Alternative 12-hour cycles of wetting and drying were also applied to simulate the effects of tidal zone and to accelerate the process of deterioration. The ratio of the sea water volume to the total exposed surface was kept constant at 10 cm<sup>3</sup>/cm<sup>2</sup>.

Compressive strength, weight, and length changes of the specimens were monitored and considered for evaluating the extent of deterioration. In order to evaluate the effect of spent catalyst on capillary and gel porosity of 28-cured cement paste, mercury intrusion porosimetry analyses were performed on paste specimens prepared from mixes containing 0 and 30 wt. % spent catalyst. The porosity of the samples was determined by means of mercury porosimetry with the use of an AUTOPORE porosimeter. Laboratory technique of X-ray diffractometry (Cu K $\alpha$  radiation, JEOL JDX-8030) was also used to study the deteriorated specimens. The tests were run in a 2 $\theta$  range of 5 - 65° at a scanning rate of 2°/min, with a deliverance slit of 1°, an anti-scatter slit of 1°, and a receiving slit of 0.01 mm. Deteriorated specimens were also examined through scanning electron microscopy and microanalysis (SEM & EDAX) after 40 weeks of exposure, using CAMBRIDGE STEREOSCAN 360 scanning electron microscope. For SEM studies, a number of deteriorated specimens were cut into halves to expose a suitable cross section of the deteriorated layer. The suitable halves were then coated with a thin layer of gold.

## RESULTS AND DISCUSSION

The results of compressive strength measurements are shown in Figures 3 and 4. As seen in Figure 3, all specimens kept in tap water show increased compressive strengths with time. Compared to plain cement, mixes with 10 and 20 wt. % replacements exhibit higher compressive strengths at all the ages. The mix containing 30 wt. % spent catalyst also exhibit considerably higher compressive strengths at ages longer than 20 weeks. These higher compressive strengths even at relatively high replacement levels confirm the effective progress of pozzolanic reactions resulting in the formation of additional calcium-silicate-, and/or calcium aluminosilicate-hydrates. These secondary reaction products are the principal binding compounds responsible for the increase in the mechanical strength of the blended cement pastes compared to reference paste [1, 4].

Specimens of all the four cements exposed to sea water show considerably reduced compressive strengths, as seen in Figure 4. The important points, however, are the beginning time for compressive strength reduction and the extent of deterioration. As seen in Figure 4, the compressive strength of the plain cement increases significantly until 8 weeks from the beginning of the exposure time and after that reduces gradually. The mix

containing 10 wt. % spent catalyst shows a small increase in compressive strength during the first 8 weeks of the exposure time followed by a significant loss of compressive strength. Specimens of the mixes containing 20 and 30 wt. % spent catalyst are subjected to loss of compressive strength even during the first 8 weeks of exposure time.

A comparison of the compressive strengths both at early and late ages of exposure shows that the mix containing 10 wt. % spent catalyst provides the highest resistance against sea water attack. Compared to Portland cement paste, the RFCC-containing pastes exhibiting higher compressive strengths in tap water especially at later ages, therefore, behave differently in sea water depending on the replacement level.

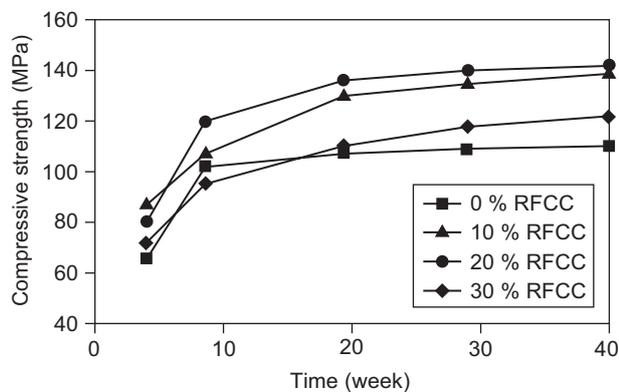


Figure 3. Compressive strength versus time for specimens kept in tap water.

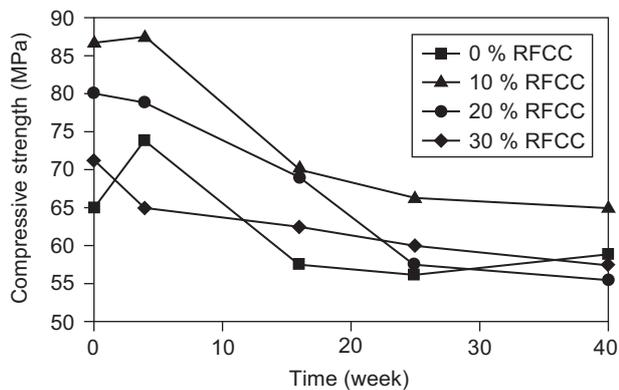


Figure 4. Compressive strength versus exposure time for specimens exposed to sea water.

These significant differences in compressive strength behavior and sea water resistance of the studied cement mixes are due to changes brought about in both their composition and permeability by partial replacement with spent catalyst. Regarding our previous work [5], experimental results clearly reveal that both water absorption and permeable pore volume of hardened paste increase as cement is replaced by RFCC spent catalyst. The higher the replacement level, the higher

the permeable pore volume and water absorption. The increase in the permeable pore volume originates from the porous microstructure of the spent catalyst. The highly porous microstructure of the spent catalyst from one side provides a much larger surface area for pozzolanic reactions significantly enhancing the pozzolanic properties of the material and from the other side results in an increase in the total permeable pore volume of the hardened paste. Figure 5 shows the distribution of the capillary and gel pores in the samples analyzed by mercury intrusion porosimetry. Considering the pore volume under  $0.05 \mu\text{m}$  as the gel porosity and the pore volume within the pore range of  $0.05 - 0.3 \mu\text{m}$  as the capillary porosity, it is seen that the incorporation of 30 wt. % spent catalyst produces a big difference in the distribution of the capillary and gel pores. It reduces the capillary porosity at the expense of a much more significant increase in the amount of gel porosity. Capillary porosity is reduced by almost 34 %, whereas gel porosity is increased by about 43 %. The higher rate of deterioration of specimens incorporating 30 wt. % spent catalyst can probably be attributed to their significantly increased gel porosity in addition to the compositional changes brought about by replacement. It must be noted however that gel pores are less permeable than capillary pores. If the role of gel pores in deterioration can be considered into account, then it means that when specimens are exposed to sea water, two different mechanisms are in action in contrary to each other; effective progress of the pozzolanic reactions and intensified deterioration due to enhanced ingress of sea water ions.

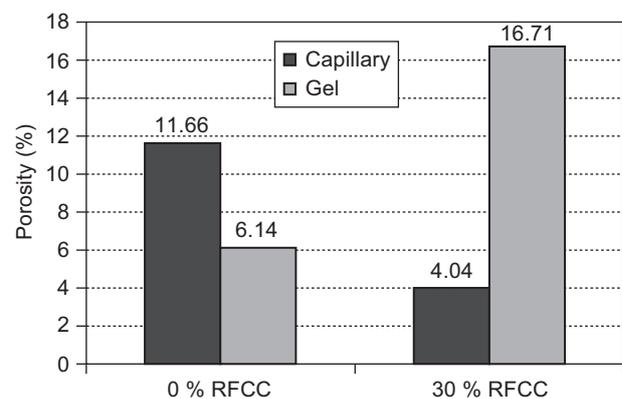


Figure 5. Distribution of capillary and gel pores in 28-day cured paste specimens.

It should be noted that compositional changes brought about by replacement could also be responsible. Reduced contents of hydraulic phases, e.g. alite and belite, result in lower early mechanical strengths (28-day compressive strengths). It is also well known that the compressive strength reduction in sea water is due to chemical reactions between calcium hydroxide of the cement phases and aggressive soluble salts of sea

water. Magnesium chloride and magnesium sulphate of sea water diffuse through inter-linked open pores of the hardened cement paste and react with calcium hydroxide. These reactions result in the formation of calcium chloride, gypsum, and magnesium hydroxide. Calcium chloride is highly soluble and is leached out of the cement paste. In the presence of chlorine in sea water, gypsum is also soluble and is leached out of the cement paste easily. Magnesium hydroxide, however, is not soluble and precipitates on the exposed surface of the paste producing a layer of brucite. Formation and leaching of calcium chloride and gypsum in paste specimens of higher porosity therefore continues auto-genously especially under the effect of wetting and drying cycles. These continued chemical reactions can also result in the depletion of calcium hydroxide in the cement paste. Excessive reduction in pH value of the pore solution due to depletion of calcium hydroxide can result in dissolution of calcium silicate hydrates of the cement paste [6-10].

The results obtained from weight measurement are presented in Figure 6. As seen, in all the cases the weight changes follow a very similar pattern. The weight of the specimens increase relatively fast until the 7<sup>th</sup> week of the exposure time. From 7<sup>th</sup> week to the 22<sup>nd</sup> week of the exposure time, all the specimens still show increases in weight, but gradually. The weight gain up to 22<sup>nd</sup> week of the exposure time is due to formation of a surface layer of brucite, i.e. magnesium hydroxide, and also precipitation of Friedel's salt [6-10]. After the 22<sup>nd</sup> week of the exposure time, all the specimens are subjected to gradual weight losses with time. Based on visual observations, these weight losses can be attributed to both spalling of small pieces from the brucite layer and accelerated leaching of calcium chloride and gypsum. The formation of the brucite layer can be monitored by simply visualizing the changes happening in the appearance of the specimens. The formation of the layer starts at some points of the exposed surfaces with nucleation of magnesium hydroxide. This layer grows gradually and covers all the faces of the specimens.

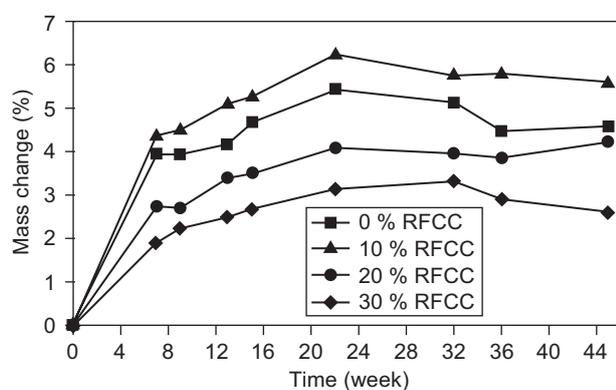


Figure 6. Weight changes versus exposure time for specimens exposed to sea water.

Continued growth then results in swelling of the layer at some points and finally separation and spalling of small pieces.

The mix containing 10 wt. % spent catalyst shows the maximum weight increase during the first 26 weeks of the exposure time. Higher replacement levels result in lower weight increase in the same time period so that the minimum weight increase corresponds to the mix containing 30 wt. % spent catalyst. The lower weight increase at relatively higher replacement levels, higher than 20 wt. %, is attributed to the consequence of more effective pozzolanic reactions. More effective pozzolanic reactions at relatively higher replacement levels significantly reduce the calcium hydroxide content of the cement paste. In fact, a larger part of the calcium hydroxide content of the cement paste is chemically fixed in pozzolanic reactions leaving behind a smaller part for taking part in the deteriorating reactions with sea water ions which in turn results in lower depositions of Friedel's salt and brucite layer.

According to the literature, hardened cement paste exhibits expansion characteristics in sea water [7, 11]. This expansion has been attributed to the formation of brucite layer on the exposed surfaces and crystallization of Friedel's salt in pore structure. Any factor influencing the formation of Friedel's salt and brucite layer can contribute in the expansion behavior of the hardened cement paste. On one hand, the formation of Friedel's salt is influenced with the concentration of the reacting constituents including Portlandite and  $C_3A$  of the cement and also chloride ions of the sea water. On the other hand, the formation of Friedel's salt can be greatly influenced by the porosity of the hardened cement paste. The presence of pozzolanic materials in cement improves both strength and durability due to additional reduction in capillary porosity during hydration caused by formation of secondary calcium silicate hydrates. If chlorine diffuses at relatively low concentrations, then pozzolanic reaction may progress enough to effectively reduce the permeability of the hardened cement paste inhibiting the extent of deterioration. Relatively high

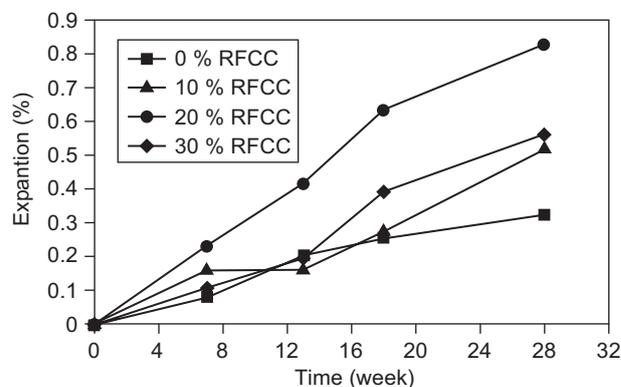


Figure 7. Length changes versus exposure time for specimens exposed to sea water.

replacement levels with a pozzolanic material exhibiting strong pozzolanic properties may also produce enough secondary calcium silicate hydrates and result in effective densification soon before any deterioration occurring. In the case of highly porous pozzolanic material, e.g. RFCC spent catalyst, the situation however is very different and complex. Two influencing factors including strong pozzolanic property and highly porous microstructure are oppositely at work.

The results of expansion measurements are presented in Figure 7. As seen, all the specimens undergo expansion during the first 28 weeks of exposure time. The amount of expansion, however, differs with replacement level. The plain cement and the mix containing 20 wt. % spent catalyst show the minimum and the maximum expansion values during the first 28 weeks of the exposure time. Mixes with 10 and 30 wt. % replacements show an almost equal expansion of moderate value.

In the case of hardened cement pastes of relatively low porosity, the Friedel's salt formation is limited to the surface layers causing proportionally lower expansion values. For hardened cement pastes of relatively higher porosity, the situation is different. On one hand, not only surface layers, but also internal layers are also included in the Friedel's salt formation producing a tendency for proportionally higher expansion values and on the other hand, higher pore volumes provide more spaces for deposition and crystallization of Friedel's salt resulting in lower tendency for expansion characteristics.

A simple comparison of the results shows that the changes in length, weight, and compressive strength of the specimens are not in harmony with each other considering the order of deterioration severity. This is due to complications brought about by opposite consequences of pozzolanic properties and highly porous microstructure of the RFCC spent catalyst.

Figure 8 shows X-ray diffractograms of the hardened pastes of plain cement (A) and the mix containing 20 wt. % RFCC spent catalyst (B) after 40 weeks of exposure to sea water, respectively.

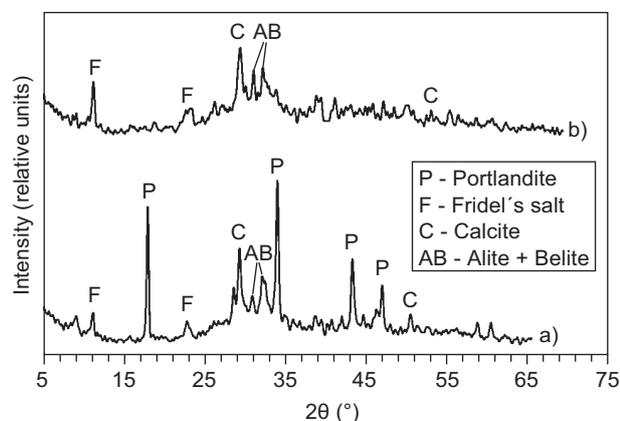


Figure 8. X-ray diffractograms of the hardened plain cement paste (a) and the hardened paste of the mix containing 20 wt. % RFCC spent catalyst (b) after 40 weeks of exposure to sea water.

posure to sea water, respectively. As seen, the pattern of plain cement shows the presence of Portlandite, calcite, a few alite, and some Friedel's salt. The phases present in the RFCC-containing mix, however, include calcite ( $\text{Ca}(\text{OH})_2$ ), alite ( $3\text{CaO}\cdot\text{SiO}_2$ ), beliet ( $2\text{CaO}\cdot\text{SiO}_2$ ), and Friedel's salt ( $\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl},\text{OH})\cdot 2\text{H}_2\text{O}$ ). The major phase in plain cement is Portlandite and in RFCC-containing mix is calcite.

The depletion of Portlandite in RFCC-containing mix can be attributed not only to the progress of pozzolanic reactions during 40 weeks, but also to its reaction with atmospheric carbon dioxide resulting in the formation calcite as a secondary reaction product and also with  $\text{C}_3\text{A}$  of the cement and chloride ions of the sea water resulting in the formation Friedel's salt. The relatively higher amount of Friedel's salt in RFCC-containing mix is due to its higher permeability allowing faster diffusion of chlorine ions and therefore formation of higher amounts of Friedel's salt.

Figures 9 and 10 represent SEM micrographs and EDAX elemental profiles of the hardened pastes of plain cement and the mix containing 20 wt. % RFCC spent catalyst prepared from the middle regions of the specimens after 40 weeks of exposure to sea water, respectively. As seen, the elemental composition of the plain cement consists of mainly calcium with few amount of silicon. The presence of chlorine can also be confirmed by the appearance of a small peak, but there is no sign from the other sea water ions. In the case of RFCC-containing mix, the appearance of additional peaks corresponding to sulphur and magnesium confirm the higher permeability of the paste enabling not only chlorine ions, but also  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$  ions of relatively lower diffusivity to permeate into the middle regions of the specimen.

The SEM micrographs and EDAX elemental profiles of the hardened pastes of plain cement and the mix containing 20 wt. % RFCC spent catalyst prepared from regions close to the exposed surfaces of the specimens after 40 weeks of exposure to sea water are represented in Figures 11 and 12, respectively. The elemental composition of the hardened pastes at regions close to the exposed surfaces are similar to corresponding compositions obtained for middle regions, except the appearance of magnesium. In the case of RFCC-containing paste, the amount of silicon has also been significantly increased. The appearance of magnesium and the increase in silicon concentration at this region can probably be attributed to the magnesium sulphate attack. The deterioration caused by this salt and decomposition of C-S-H gel to M-S-H, which does not possess cementing properties, can be a probable reason for this phenomenon. The formation of magnesium silicate hydrate in different types of Portland cement mortars exposed to magnesium sulphate has been reported by Gollup and Taylor [8]. A number of researchers [9, 10] have also reported formation of the same hydrate in case

of concretes exposed to sea water. They have illustrated that formation of Mg-rich phases is normally associated with the neat surface regions of concrete.

Figures 13 and 14 represent SEM micrographs of brucite surface layers formed on exposed surfaces of the hardened pastes of plain cement and the mix containing 20 wt. % RFCC spent catalyst after 40 weeks of exposure

to sea water, respectively. The brucite phase however was not present in the X-ray diffractograms shown in figure 8. It must be noted that this phase forms as an external thin layer on the exposed surfaces of the cement paste. The sampling for X-ray diffractometry therefore must include enough materials from surface regions to represent the brucite phase.

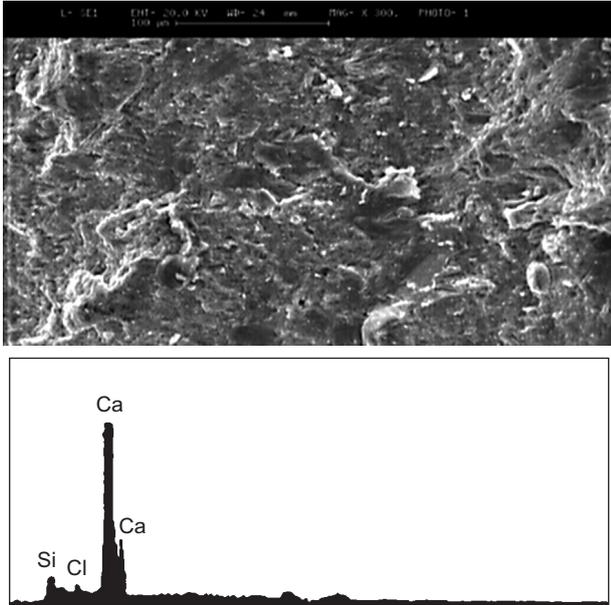


Figure 9. SEM micrograph and EDXA elemental profile of the hardened pastes of plain cement prepared from middle region of the specimen after 40 weeks of exposure to sea water (magnification: 300 $\times$ ).

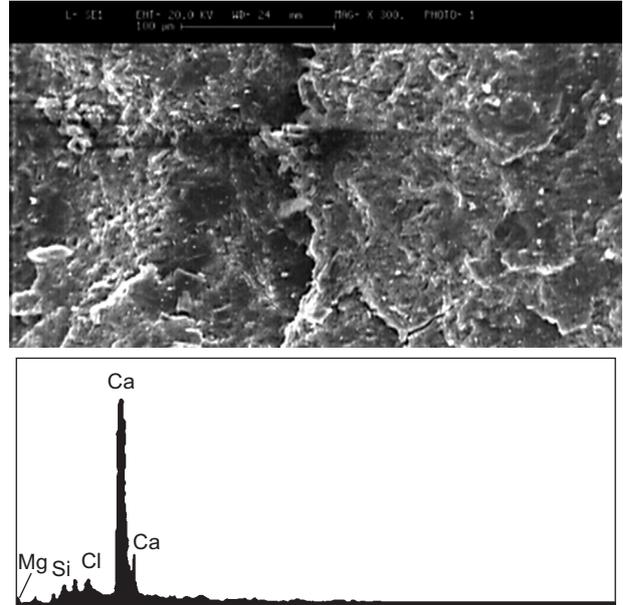


Figure 11. SEM micrograph and EDXA elemental profile of the hardened pastes of plain cement prepared from regions close to the exposed surfaces of the specimen after 40 weeks of exposure to sea water (magnification: 300 $\times$ ).

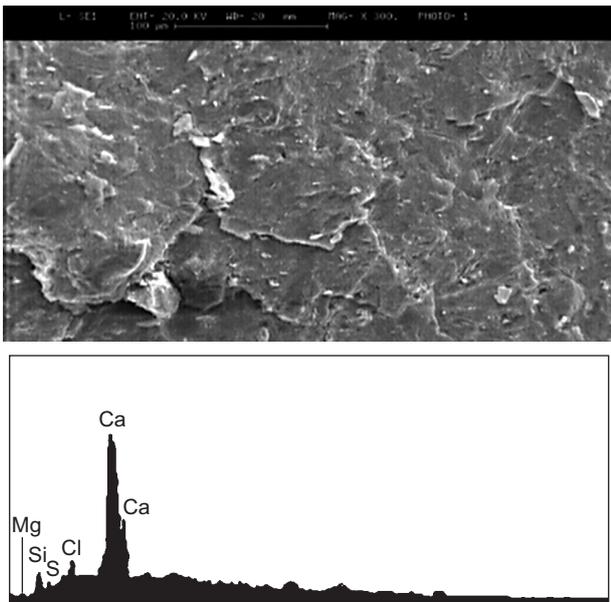


Figure 10. SEM micrograph and EDXA elemental profile of the hardened pastes of the mix containing 20 wt. % RFCC spent catalyst prepared from middle region of the specimen after 40 weeks of exposure to sea water (magnification: 300 $\times$ ).

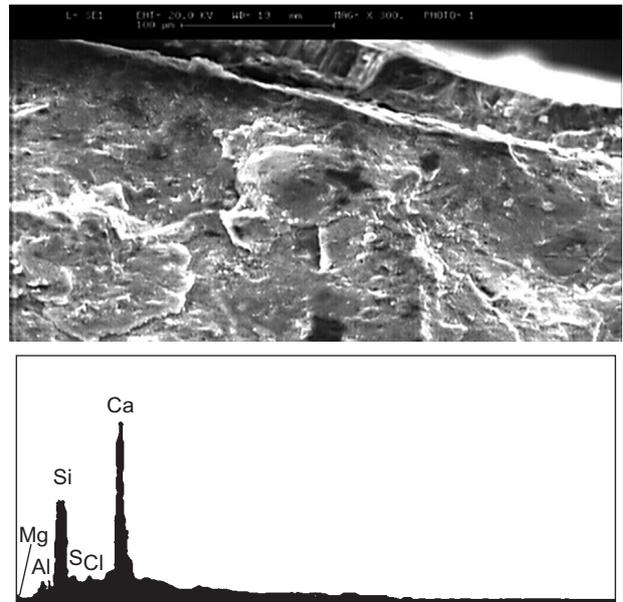


Figure 12. SEM micrograph and EDXA elemental profile of the hardened pastes of the mix containing 20 wt. % RFCC spent catalyst prepared from regions close to the exposed surfaces of the specimen after 40 weeks of exposure to sea water (magnification: 300 $\times$ ).

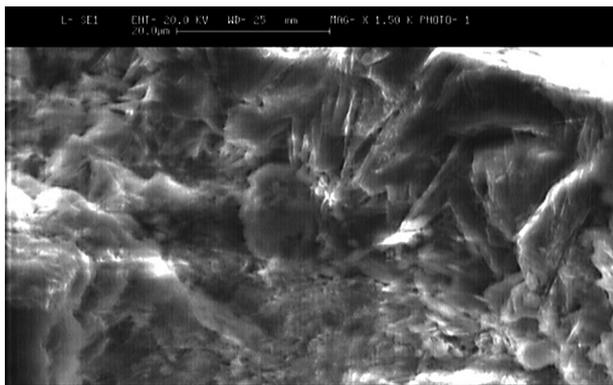


Figure 13. SEM micrograph of brucite surface layer formed on exposed surfaces of the hardened paste of plain cement after 40 weeks of exposure to sea water (magnification: 1500 $\times$ ).

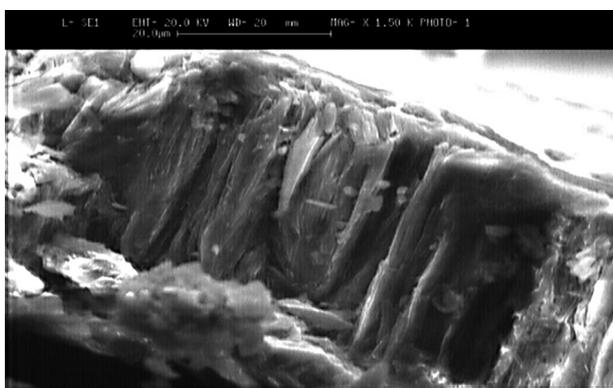


Figure 14. SEM micrograph of brucite surface layer formed on exposed surfaces of the hardened paste of the mix containing 20 wt. % RFCC spent catalyst after 40 weeks of exposure to sea water (magnification: 1500 $\times$ ).

## CONCLUSION

RFCC spent catalyst that is mainly made up of silica and alumina is a relatively high quality pozzolnic material. Experimental results show that the mix containing 10 wt. % spent catalyst provides the highest resistance against sea water attack. Specimens of the mix containing 20 wt. % spent catalyst showing increased compressive strengths in tap water are subjected to

significant loss of compressive strength even during the first 8 weeks of exposure to sea water. All the specimens show weight gain up to 22<sup>nd</sup> week of the exposure time due to formation of a surface layer of brucite and also precipitation of Friedel's salt. After that spalling of small pieces from the brucite layer and accelerated leaching of calcium chloride and gypsum result in some gradual weight losses. All the specimens undergo expansion during the first 28 weeks of exposure time with the plain cement and the mix containing 20 wt. % spent catalyst exhibiting the minimum and the maximum expansion values. A simple comparison of the results shows that the changes in length, weight, and compressive strength of the specimens are not in harmony with each other considering the order of deterioration severity. This is due to complications brought about by opposite consequences of relatively strong pozzolanic properties and highly porous microstructure of the RFCC spent catalyst. These results prove the important role of the permeability of the cement-based materials as a durability determining factor and the fact that higher compressive strengths do not necessarily result in better durability performances.

## REFERENCES

1. Payá J., Monzó J., Borrachero V.M., Velázquez S.: *Cem. Concr. Res.* **33**, 603 (2003).
2. Pacewska B., Bukowska M., Wilinska I., Swat M.: *Cem. Concr. Res.* **32**, 145 (2002).
3. Payá J., Monzó J., Borrachero V.M.: *Cem. Concr. Res.* **29**, 1773 (1999).
4. Jung-Hsiu Wu, Wan-Lung Wu, Kung-Chung Hsu: *Cem. Concr. Res.* **33**, 245 (2003).
5. Allahverdi A., Vakilinia S., Gharabeglu P.: *Ceramics-Silikaty* **55**, 161 (2011).
6. O'Farrel M., Wild S., Sabir B.B.: *Cem. Concr. Res.* **30**, 757 (2000).
7. Al-AMoudi O.S.B.: *Adva. Cem. Res.* **14**, 89 (2002).
8. Gollup R.S., Taylor H.F.W.: *Cem. Concr. Res.* **22**, 1027 (1992).
9. Cole W.F.: *Nature*, **171**, 354 (1953).
10. Roy D.M., Sonnenthal E., Prave R.: *Cem. Concr. Res.* **15**, 912 (1985).
11. Santhanam M., Cohen M., Olek J.: *Cem. Concr. Res.* **36**, 2132 (2006).