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Cement and Concrete Composites

Elixir Cement & Con. Com. 47 (2012) 8866-8873

ISSN: 2229-712X

Utilization of soda ash plant solid wastes in manufacture of cement

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ARTICLE INFO

Article history:
Received: 7 April 2012;
Received in revised form: 18 May 2012;
Accepted: 12 June 2012;

Keywords
Waste utilization;
soda ash;
cement;
micro-concrete;
Solvay process

ABSTRACT

Different from other soda ash plants based on Solvay Process in the world, Mersin Soda plant applies a particular process in order to decrease the chloride concentration of the solid waste. The purpose of the current study is to investigate utilization of this solid waste with low chloride content in possible industrial applications. It is determined that using solid waste as a mineral additive in some of the cements produced in Mersin-Adana region, slightly reduces consistency of mortar and shortens setting time. However consistency and setting time of the samples including solid waste can be increased to the levels of the reference sample by using 0.05% of retarding admixture. It is observed that compressive strength of samples with 5% waste is similar to the reference sample. As a result, it has been found that 5 percent solid waste can be used in the cement as a minor constitute.

Introduction

Soda ash, also known as sodium carbonate (Na_2CO_3), is a white, crystalline, hygroscopic powder. It is an important raw material to glass, soap and detergent, chemicals, paper, and water treatment industries [1]. World soda ash production capacity was 63 million tonnes/ year in 2011. Approximately 45% of world soda ash capacity is covered by synthetic Solvay process and 24% of the capacity is supplied by natural trona reserves. Currently there are around 70 soda ash plants based on Solvay process in the world [2].

Solvay Process

Solvay process uses salt, limestone, coke or anthracite as its raw materials and ammonia as a cyclic reagent. Utilities necessary for this process are natural gas (or coal) and water. Simple production process diagram can be found in Figure 1.1.

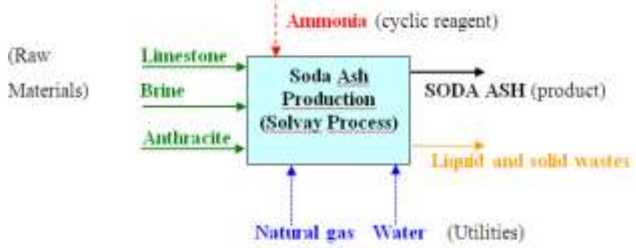

Figure 1.1 Production of soda ash based on Solvay process

The Solvay process for the production of soda ash may be summarized by the theoretical global equation involving the two main components: sodium chloride (salt) and calcium carbonate (limestone).

$$2\,NaCl + CaCO_3 \longrightarrow Na_2CO_3 + CaCl_2$$

(salt) (limestone) (soda ash) (calcium chloride in liquid waste)

In practice it is not possible to produce soda ash by the overall reaction given above. Participation of other substances and many different process steps are required. In the first step, ammonia (NH_3) is absorbed (1) and then, the ammoniated brine is reacted with carbon dioxide (CO_2) to form successive intermediate compounds: ammonium carbonate (2) then ammonium bicarbonate (3). Precipitation of sodium bicarbonate is achieved and ammonium chloride (4) is obtained by continuing CO_2 injection and cooling the solution. Main chemical reactions of the process are given below.

$$NaCl\,(aq) + H_2O\,(l) + NH_3\,(g) \leftrightarrow NaCl\,(aq) + NH_4OH\,(aq) \quad (1)$$

$$2NH_4OH\,(aq) + CO_2\,(g) \leftrightarrow (NH_4)_2CO_3\,(aq) + H_2O \quad (2)$$

$$(NH_4)_2CO_3\,(aq) + CO_2\,(g) + H_2O\,(l) \leftrightarrow 2\,NH_4HCO_3\,(aq) \quad (3)$$

$$2NH_4HCO_3\,(aq) + 2NaCl\,(aq) \leftrightarrow NaHCO_3\,(s) + 2NH_4Cl\,(aq) \quad (4)$$

Sodium bicarbonate crystals are separated from the mother liquor (4) by filtration, then sodium bicarbonate is decomposed thermally into sodium carbonate, water, and carbon dioxide (5). CO_2 is recovered in the carbonation step (equations 2 and 3 above).

$$2\,NaHCO_3\,(s) \rightarrow 2\,Na_2CO_3\,(s) + H_2O\,(l) + CO_2\,(g) \quad (5)$$

The mother liquor (4) is treated with steam and alkali (generally calcium hydroxide suspension called as milk of lime) to recover ammonia (6). Gaseous NH_3 obtained as a result of this distillation process is recycled to the absorption step (equation 1 above). The outlet solution of the distillation process contains dissolved calcium chloride and all the residual solid materials.

$$2\,NH_4Cl\,(aq) + Ca(OH)_2\,(aq/s) \rightarrow CaCl_2\,(aq) + 2\,NH_3\,(g) + 2\,H_2O \quad (6)$$

Carbon dioxide and calcium hydroxide originate from limestone calcination (7) followed by calcium oxide hydration (8).

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \quad (7)$$

$$CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(aq/s) \quad (8)$$

Brine (NaCl) has to be treated before being input into the process to remove calcium and magnesium ions which would otherwise react with alkali and carbon dioxide to produce insoluble salts contributing to scale formation inside the equipments. Brine purification reactions are described in the following equations:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\,(s) \quad (9)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\,(s) \quad (10)$$

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Solid Wastes of the Solvay Process

The liquid phase coming out of the distillation unit (distiller effluent) contains unreacted sodium chloride (reaction (4) is not complete due to thermodynamic and kinetic limitations) and calcium chloride obtained as a result of reaction (6). Solid matter of the distiller suspension derives primarily from the original limestone and a small quantity of lime maintained in an excess that can ensure a total decomposition of NH_4Cl.

The total quantity and composition of the solid wastes depend on the composition of the raw materials. Solid waste contains calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$), magnesium hydroxide ($Mg(OH)_2$), calcium hydroxide (CaO), silica (SiO_2) and alumina (Al_2O_3) components. The average solid content of the distiller effluent is estimated to be 240 kg/t soda ash produced.

The type of effluent treatment for the suspended solids depends on the local conditions and regulations. Some of the synthetic soda ash producers in Europe discharge their distiller effluent directly to the sea. There are also some plants discharging liquid waste to the sea or river after separating the solid particles in the settling ponds. Settling ponds are abandoned and replanted for daily usage when filled with solid particles [1]. Different from other soda ash plants, Mersin Soda plant applies a special process in order to decrease the chloride concentration of the solid waste.

Utilization of Solid Wastes of the Solvay Process in Cement or Concrete Industries

Numerous studies have been carried out in order to recover the suspended material of the distiller effluents. Because of the moisture content, solid wastes of the soda ash plants contain also sodium chloride and calcium chloride restiricting the utilization areas. Removal of this salt content is the major difficulty to overcome. The second difficulty is to dry the material to an acceptable level of residual moisture for transportation and re-use [1].

Information about utilization of soda ash solid waste for neutralisation of acidic soil, production of binding material, portland cement, alinite cement, concrete block, brick and road coating materials can be found in literature. Some of the studies are summarized below.

- Yeginobali Asim, investigated suitability of using solid waste of the soda ash plant instead of lime in the production of plaster and masonry mortar and sandlime bricks. He published his findings as an article in 1990. He used solid waste of the Mersin Soda plant in his experiments. (Chloride concentration of the solid wastes was high since chloride reduction process was not available at that time.)

As a result of that study it was found that solid waste had hydraulic properties and could be used in the production of plaster and masonry mortar and sandlime bricks having reduced strengths. It was stated that potential utilization areas of soda waste would increase if the chloride concentration had been decreased [3].

- Sharma et al. blended 35-55 % of soda solid waste with bauxite, limestone and sandstone and burned at varying temperatures for various periods. It was reported that burn ability of all samples was good at 1400 ºC. But 35% of solid waste was found suitable for clinker production by considering the chloride content.

Compressive strength and other properties of the clinker and cement samples produced from soda ash waste were found to be suitable to IS:269:1989 [4].

- Kuznetsova et al. used soda ash solid waste for sulfo-ferrit clinker production. Calcium sulphate content of soda ash solid waste reduced the amount of gypsum required. As a result, using cement containing sulfo-ferrit was found to be appropriate for high quality and non-shrinking oil well cement. On the other hand it was specified that sulfo-ferrit clinker amount must not be more than 10%. Laboratory studies were confirmed by pilot studies [5].
- Verlaeten et al. studied for using soda ash solid waste to produce hydraulic mortar or concrete by mixing with blast furnace slag, sand or fly ash, aluminium (dust) and water [6].

Material and Methods

Aim, Content, Programme

The aim of this study is to investigate the potential of using the waste in manufacture of cement and concrete.

Because of its fineness and chloride content, it is expected that the waste will increase the requirement of water for a certain consistency and lead to earlier initial set. Since the consistency is not taken into consideration in cement experiments done according to TS EN 196-1 standard [7]; instead of producing norm mortar including 450 g cement, 225 g water and 1350 g norm sand, producing mortar that would allow the observation of the changes in consistency by making use of increments in water content was preferred. In order to distinguish this mortar from “norm mortar” it was preferred to name it as “micro-concrete”.

At first stage experiments, 0, 5, 10, 15, 20 % dry waste was used in place of CEM I 42.5 R cement; 450 g (cement + waste), 1350 g norm sand and exclusively, in order to make it possible to observe the changes in consistency, 310 g water was used; setting times, flow diameters and 1, 7, 28-days compressive strengths were measured. The series including waste was repeated as the first one would include the same amount of water while the other one’s water content was increased so as to acquire equal flow diameter (consequently equal consistency).

At second stage experiments, in order to observe the possible influence of cement types, two different types of cements were also investigated in terms of same parameters by producing series with 0, 5, and 20 % substitution ratios.

According to the results of the initial two stages, 5-10% substitution of the waste would not have considerable adverse influence on the compressive strength, would decrease the setting times and slightly increase the requirement of water. On account of this, at third stage experiments two different CEM I and CEM II cements were used to produce 5% substituted micro-concretes, and it was aimed to turn back to the set values and flow diameters of the “reference mortar including the waste” by adding retarding admixture or plasticizer at various ratios. Since the Standard restricts the minor component amount with 5%, the substitution ratio was selected accordingly and 10% substitution was not included.

At fourth stage; reference, 5% waste substituted (without admixture) and 5% waste substituted (with admixture) norm mortars were produced by using two most common cements in region; setting times, 2, 7, 28-days compressive strengths were measured.

Experimental

CEM I and CEM II cements obtained from two different manufacturers, CEN norm sand obtained from Set Çimento San. and Tic. A.Ş. Trakya Cement Plant and distilled water were used in experiments. Chemical and X-ray fluorescence spectrometer (XRF) analysis of the solid wastes was also performed before the experiments. The soda plant waste that originally contains 50-60 % moisture was dried before usage.

Production of Micro-Concrete

Micro-concrete is defined as the concrete of which the coarse aggregates are dismissed. The procedure for preparation of the mortar used in micro-concrete experiments by using cement, norm sand, distilled water and solid waste in cement mixed is specified [8]:

- Weigh the materials.
- First add the sand and optionally the waste, mix for 15 sec.
- Add 1/3 of the water, mix for 45 sec.
- Wait for 3.5 minutes. Add the cement. Wait for 0.5 min. more.
- After this 5 min. period mix for 1 min. more.
- After adding water, mix for 1 min.
- Finally mix at high speed for 1 min. more.

After measuring the consistency of the prepared mortar, it is placed in the three-gang mould that has 4x4x16 cm sizes by tamping with a steel rod for a defined number of times and the mould is stored in a room at 20 ^{o}C for one day after covering the top with glass to prevent loss of water. Three samples are used to measure compressive strength. Consequently, the mortar is prepared three times to enable the measurement of 1, 7, 28-days compressive strengths. After one day, all of the three-gang moulds are opened and the compressive strength of one sample from each of the mould is measured. The other specimens that will be used in measuring 7-days and 28-days compressive strengths are kept in water at 20 ^{o}C.

Set and Consistency Studies

Micro-concrete technique was applied in preparation of mortars used in set and consistency studies. In order to measure consistency, a specially made flow funnel resembling a truncated cone of 5 cm upper diameter, 10 cm lower diameter and 15 cm height was used. The fresh mortar was placed in the flow funnel as described in Figure 3.1 and after lifting the funnel the extent of the flow was measured. The measured diameter was recorded as the consistency of the mortar [8].

Figure 3.1 Determining consistency of micro concrete

Figure 3.2 Measuring initial and final set of micro concrete

The setting times of the samples were measured with concrete-set-apparatus, regarding to TS 2987 standard [9]. Accordingly, a mortar prepared so as to have 16-18 cm consistency was placed in a cylindrical ring of 7.5 cm inner diameter, 8.5 cm outer diameter and 5 cm height by tamping with a spatula. Top of the ring was covered with glass and kept at 20 ^{o}C. As shown in Figure 3.2 the ring full of mortar was taken on the balance of the concrete-set-apparatus periodically and the arm was pulled so that the probe that is 2.5 cm in length will completely driven into the mortar. The value of 1 N/mm^2 measured at the balance was accepted as the initial set and 4 N/mm^2 as final set. Since 1 kg is equal to 10 N and the area of the probe of the concrete-set-apparatus is 0.27 cm^2; when the value read at the balance reaches 2.7 kg it is taken as initial set and when the value reaches 10.8 kg it is taken as final set.

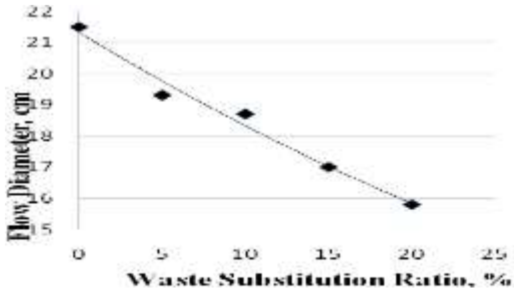

Figure 4.1 Effect of waste substitution on consistency (at constant water content)

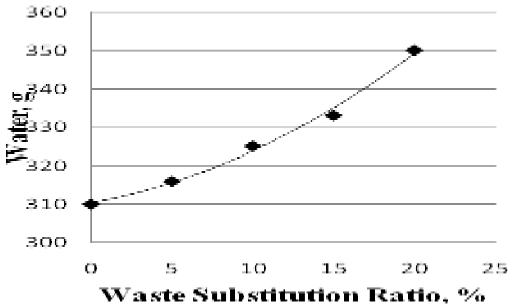

Figure 4.2 Effect of waste substitution on water requirement (at constant consistency)

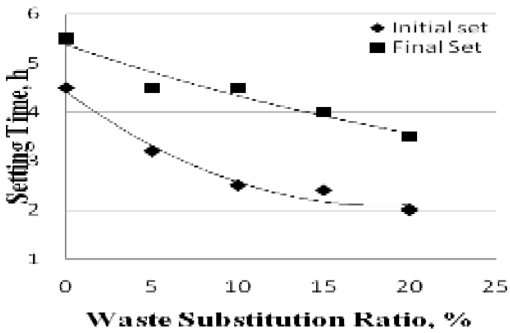

Figure 4.3 Effect of waste substitution on setting time (at constant water content)

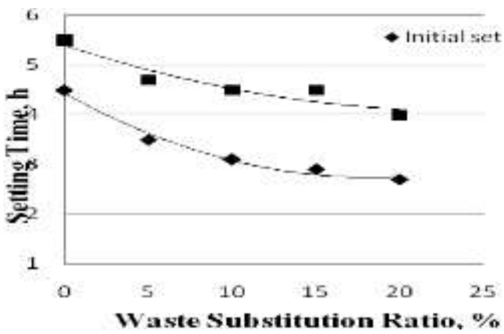

Figure 4.4 Effect of waste substitution on setting time (at constant consistency)

Norm Mortar Experiments

In the studies done in accordance with TS EN 196-1, the reference sample was prepared by using 450 g cement, 225 g water, and 1350 g norm sand. However, 427.5 g cement, 22.5 g dry waste, 225 g water and 1350 g norm sand were used for the cases that the cement was substituted with waste at 5% ratio. In addition, the experiment that includes substitution of the cement with waste was repeated by using retarder.

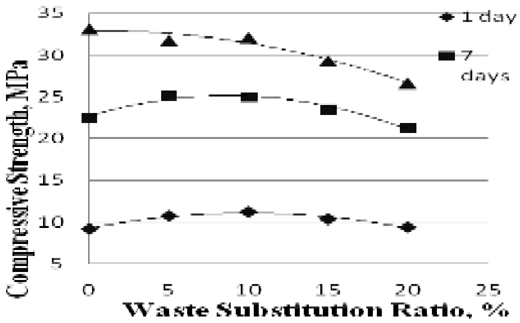

Figure 4.5 Effect of waste substitution on compressive strength (at constant water content)

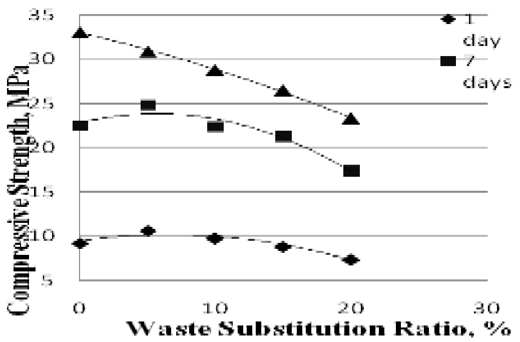

Figure 4.6 Effect of waste substitution on compressive strength (at constant consistency)

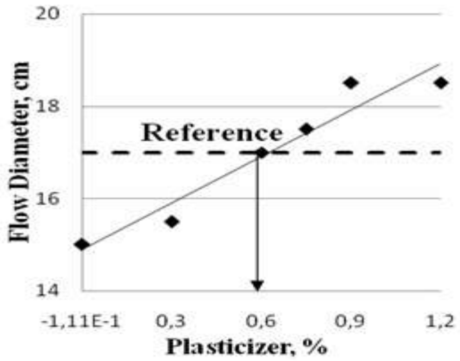

Figure 4.7 Effect of plasticizer on consistency (A CEM I 42.5 R)

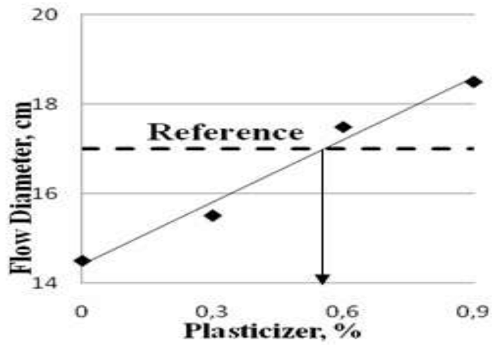

Figure 4.8 Effect of plasticizer on consistency (B CEM II 32.5 R)

Other Analysis

In order to have relative information about the pozzolanic activity of the waste, the activity index of the waste was determined in accordance with TS EN 450-1 standard [10].

TS EN 196-3 standard [11] was used to determine whether the waste have adverse effect on the volume expansion or not. The expansion experiment was applied to the sample in which the cement was substituted with waste at 5% ratio.

The chloride contents of the cements used were determined in accordance with TS EN 196-21 standard [12].

The fineness values (Blaine) of the cements were measured with Wasagchemie brand Blaine-Star Zeb model instrument. XRF analysis was conducted with Thermo brand ARL ADVANT'X 543 model instrument.

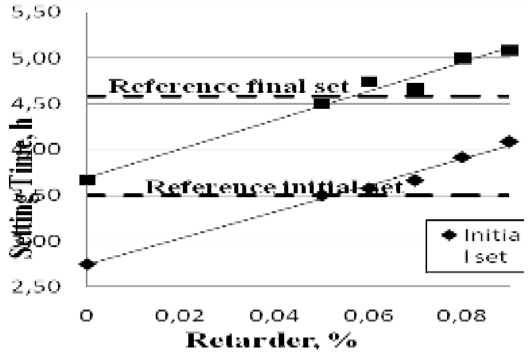

Figure 4.9 Effect of retarder on setting time (A CEM I 42.5 R)

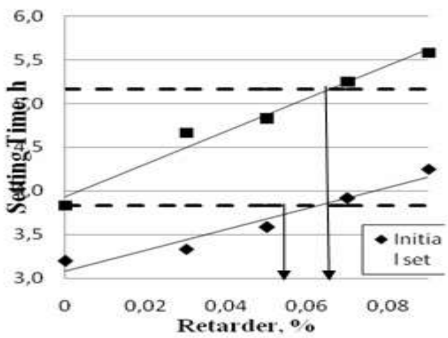

Figure 4.10 Effect of retarder on setting time (B CEM II 32.5 R)

Results and Discussions

In this section, the micro-concrete and norm-mortar studies comprising the substitution of the cements manufactured in Adana-Mersin region, and the consistency and set experiments' results are given in detail.

Chemical analysis of a typical solid waste of the soda plant is shown in Table 4.1. X-ray fluorescence spectrometer (XRF) analysis results are given in Table 4.2. Blaine fineness value of solid waste (specific surface area) is about 5000 cm^2/g.

Micro-Concrete Experiments

Results of the experiments comprising substitution of cement with waste is given in Table 4.3. CEM I 42.5 R cement with 3790 cm^2/g Blaine (fineness) value acquired from the manufacturer A, distilled water, dried waste containing 1.1 % chloride on dry basis, and standard sand were used in these experiments.

The relationship between the waste substitution ratio and the consistency (fixed water content) is seen at Figure 4.1: as the substitution ratio increases the flow diameter continuously reduces and decreases from the value of the reference that is 21.5 cm towards the value of 15.8 cm.

Figure 4.2 shows the relationship between the waste substitution ratio and water requirement for fixed consistency. As the substitution ratio increases the water requirement for equal consistency increases as well, at 20 % substitution ratio it reaches 40 g (12.9%).

As it is expected, substitution of cement with waste that has a high fineness value decreases the consistency at equal water content and/or increases the water requirement at equal consistency. This behaviour is generally observed when mineral additives that are finer than cement is used, and the validity for silica fume and fine fly ash is known [13].

The increase of water requirement remains at a reasonable level that it can easily be regulated by using plasticizer or super-plasticizer, and it is well known that this kind of admixtures can reduce the water requirement up to 30-40%.

The effect of substitution of A CEM I 42.5 R cement with solid waste at various ratios (5, 10, 15, 20 %) on setting times is shown in Figure 4.3 where the water content is fixed and in Figure 4.4 where the consistency is kept constant. Accordingly, initial set and final set decrease as the waste percentage increases.

This is possibly because of the chloride content of waste. Generally, chlorides, especially calcium chloride, are the most efficient set accelerating admixtures; yet their usage at reinforced concrete is limited because of the risk of reinforcement corrosion.

The extent of reduction of initial set and final setting times of mortars of constant consistency is shorter than the mortars with constant water content. The reason is that, the excess water added to increase the consistency retards the set. But, the reduction of setting times seems to be easily regulatable by using retarding admixture.

The effect of substitution of cement with solid waste –at constant water- on 1, 7, 28-days compressive strengths are shown in Figure 4.5. 1-day compressive strength increases up to 10% substitution level and decreases at 15% and 20% levels; yet it still remains above the reference. 7-days compressive strength increases up to 5-10%, starts to decrease at 15% while remaining above the reference, keeps decreasing even down under reference at 20%. 28-days compressive strength slightly decreases at 5 and 10% substitution ratios, the manner of falling increases at 15%.

The high fineness and chloride content of the waste have positive influence on early strength, while increasing the substitution ratio affects the strength negatively since it decreases the cement dosage and increases water/cement ratio. These two influences can be compensated at 20% substitution ratio for 1-day strength and at 15% substitution ratio for 7-days strength; yet it cannot ever be compensated for 28-days strength, since the negative effect is so dominating that even at 5-10% substitution ratio it slightly decreases the strength.

The influence of substitution of the cement with solid waste at constant consistency on 1, 7, and 28-days strength is shown on the graph at Figure 4.6. The 1-day compressive strength increases up to 10% substitution ratio, decreases down to the same level with the reference at 15% ratio, while decreases down under the reference at 20% ratio. The 7-days compressive strength increases at 5% ratio; decrease down to the same level with reference and after 10% keeps decreasing and descends even under the reference. The 28-days strength slightly decreases for 5% substitution ratio and the decline becomes more distinguishable as from 10%.

Since the water content increases as the consistency of the mortar is kept constant, the compressive strengths are lower with respect to the experiments done under constant water. At this case, the positive influence of waste coming from its high fineness and chloride content decreases from 15% substitution ratio to 10%.

To summarize, we can conclude that, using the waste up to 10% substitution ratio to the CEM I 42.5 R cement does not have considerable negative effect on strength; even it increases the early strength.

Micro-Concrete Experiments with Different Cements

After inspecting the effect of substitution of cement with waste on consistency, setting times and compressive strength of the mortar by using A CEM I 42.5 R it is decided to investigate the effect of different cement types. In this study, B CEM II 42.5 R and B CEM II 32.5 R cements were used and the cement was substituted with waste at 5% and 20% ratio. The results of the experiments are given at Table 4.4.

First glance at Table 4.4 suggests that, for both of the cements, as the substitution ratio increases the consistency (flow diameter) at constant water decreases and/or the water requirement at constant consistency increases. This behaviour is similar to that of A CEM I 42.5 R in the same way the setting times become shorter.

At constant water/cement ratio experiments of the series 5%, 1-day strength is slightly higher than reference at constant consistency experiments. The 7-and 28-days strengths are lower for both constant water/cement ratio and constant consistency series. For 5% waste series, the loss of strength is 2.7 MPa (8.4%) and 5.2 MPa (16.2%) for B CEM II 42.5 R; it is 3.0 MPa (11.6%) and 4.5 MPa (17.4%) for B CEM II 32.5 R. If it is noted that for the 5% series of A CEM I 42.5 R the loss of strength is 1.3 MPa (3.9%) and 2.2 MPa (6.6%), it is seen that the loss is rather more.

Regulating the Consistency and Setting times of Mortar by Using Suitable Chemical Admixtures

In order to equate the consistency and setting times of the mortar prepared by substituting 5% of the cement with soda waste to the one prepared by using only cement, easily obtainable plasticizer or retarder was employed, using micro-concrete technique.

Consistency Study with Plasticizer

Return back to the level of reference was investigated by producing micro-concretes as reference with no waste, waste substituted admixture-free reference and those containing plasticizer at a ratio increasing by 0.3 like 0.3%, 0.6%, 0.9%...

The water content of the reference micro-concrete produced by using A CEM I 42.5 R and B CEM II 32.5 R type cements so that the consistency would be at 16-18 cm level was selected as 278 g (A CEM I) and 283 g (B CEM II). The percentage of the plasticizer was calculated considering the total of cement and waste amount. The results obtained are presented in Table 4.5 and Table 4.6.

As can be seen in Figure 4.7 and 4.8, it is possible to regulate the plasticity (fluidity), i.e. to equate the plasticity to that of reference without waste, by using commonly used plasticizers at low level like ~0.6%.

Set Study with Retarder

Return back to the setting times of waste-free reference was investigated by producing micro-concretes as reference with no waste, waste substituted admixture-free reference and those containing retarder at a series in between 0.03-0.09%.

The water amount of the reference mortar produced employing micro-concrete technique by using A CEM I 42,5 R and B CEM II 32,5 R type cements was selected as 298 g (A CEM I) and 283 g (B CEM I) respectively, so that the consistency is at 16-18 cm. The percentage of the retarder was calculated considering the total of cement and waste amount. The results obtained are in Table 4.7 and 4.8.

As can be seen in Figure 4.9 and 4.10; the setting times of the reference with no waste can be reached by using retarder at 0.05-0.06 % and 0.06-0.07 % levels, for the studies conducted with A CEM I 42.5 R and CEM II 32.5 R respectively.

To summarize, using considerably low amount of retarder is enough to handle the set accelerating effect of the waste. In fact, the setting times are already in between the levels suggested at the related standard. The acceleration of the set may even be a positive influence for the cements with relatively long setting times; yet if it is specially wanted it seems easy to regulate the setting times and turn them back to the reference's level.

Norm Mortar Experiments

Besides micro-concrete studies, TS EN 196-1 standard was also used to prepare samples for measuring 2, 7, 28-days compressive strengths. In these studies, A CEM I 42.5 R, A CEM II 42.5 N, B BPÇ 52.5 N-85, B CEM I 42.5 R cements were used.

The results obtained are summarized in Table 4.9. According to this:

- The setting times can be regulated by using retarder; however the dosage may differ according to the cement in charge.
- The loss of few MPa compressive strength at 28 days for the series containing 5% waste can be equated so that there was no considerable difference between compressive strengths by using 0.05% retarder.
- In short, it is possible to substitute 5% of the cement with waste.

Other Analysis

In order to have an opinion, the activity index (pozzolanic activity) of the waste was investigated for two different CEM I 42.5 R cements by means of TS EN 450-1 (Fly Ash for Concrete) standard and the data for 28-days is given at Table 4.6. Indices measured as 74% and 77% are at the boundary of 75% value proposed at the standard, and it figures out that the waste has a pozzolanic activity similar to that of the fly ash.

According to the determination of expansion performed regarding TS EN 196-3, extra expansion with respect to the reference was not observed for the series of 5% waste content.

The chloride (Cl^-) content of the cements used was determined according to the analysis performed with respect to TS EN 196-21 standard. It was seen that, the Cl^- content of the cements used vary between 0.003-0.2%. The Blaine (fineness) values of the cements were measured at Mersin Çimsa Laboratory. The results obtained are given in Table 4.11.

The additional chloride amount that will be brought about by the waste at 5% substitution ratio stays at 1.1x0.05% $\approx$ 0.05-0.06% level; so the total chloride amount does not exceed the allowed level of 0.1%.

Conclusion

Soda solid waste is a mineral additive that accelerates the set of cement as it is substituted with cement up to 10-15 % level, increases the water requirement for a specific consistency, has positive influence on early strength, and has little negative influence on 28-days strength and exhibits pozzolanic activity.

When the cement is substituted with waste at 5% ratio, it is enough to equate the setting times and strengths to the level of reference without waste by addition of a very low level amount of retarder/plasticizer such as 0.05%.

As a matter of fact, the performance is expected to rise in case of direct addition to the clinker instead of substitution with cement.

Evaluation of the soda solid waste as a minor additive at cement production will be beneficial for both environmental and economical aspects.

Further Studies

The study will continue with durability (water penetration, chloride penetration, durability against sea water at reinforced and plain concrete) investigations. Accelerated corrosion tests can be performed by using potentiostat/ galvanostat/EIS instrument. Furthermore, the opportunity of using the waste as a minor additive during grinding will be investigated with respect to technological and economical points.

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Table 4.1 Chemical analysis of a typical solid waste the Mersin Soda plant

Parameter	% On Dry Basis
Chloride (Cl^-)	1.1
Calcium Sulphate ($CaSO_4$)	5.2
Calcium Carbonate ($CaCO_3$)	70.2
Calcium Hydroxide ($Ca(OH)_2$)	12.5 *
Magnesium Hydroxide ($Mg(OH)_2$)	3.9
R_2O_3 (Fe_2O_3 + Al_2O_3)	2.9
Silicon Dioxide (SiO_2)	1.2

* Value is calculated. Amount of other calcium compounds is subtracted from result of total calcium determination.

Table 4.3 Results of experiments on substitution of solid waste in portland cement

	Waste (%)	Cement (g)	Waste (g)	Water (g)	Flow dia. (cm)	1-day comp. str. (MPa)	7-day comp. str. (MPa)	28-day comp. str. (MPa)	Setting time (hour)	
									Initial set	Final set
1	0	450	0	310	21.5	9.2	22.5	33.1	4.5	5.5
2	5	427.5	22.5	310	19.3	10.7	25.2	31.8	3.2	4.5
3	5	427.5	22.5	316	21	10.6	24.9	30.9	3.5	4.7
4	10	405	45	310	18.7	11.2	25.0	32.1	2.5	4.5
5	10	405	45	325	20.7	9.7	22.4	28.8	3.1	4.5
6	15	382.5	67.5	310	17	10.3	23.5	29.3	2.4	4.0
7	15	382.5	67.5	333	19.7	8.8	21.3	26.5	2.9	4.5
8	20	360	90	310	15.8	9.4	21.3	26.6	2.0	3.5
9	20	360	90	350	21	7.4	17.4	23.3	2.7	4

1350 g of CEN standard sand was used

Table 4.2 XRF Analysis of a typical soda plant solid waste

Parameter	Washed solid waste (%)
Free lime	0.55
CaO	48.80
SiO_2	1.85
Al_2O_3	0.67
Fe_2O_3	0.65
MgO	1.84
Na_2O	0.66
SO_3	0.81
Ignition Loss	41.7

Table 4.4 Results of experiments on substitution of solid waste in different cements (1350 g of CEN standard sand was used)

	Waste (%)	Cement (g)	Waste (g)	Water (g)	Flow diameter (cm)	1-day comp. str. (MPa)	7-day comp. str. (MPa)	28-day comp. str. (MPa)	Setting time (hour)	
									Initial set	Initial set
B CEM II 42.5 R (4950 cm^2/g)										
1	0	450	0	310	23.7	10.0	25.2	32.1	3	4
2	5	427.5	22.5	310	21.7	10.5	23.5	29.4	2.8	4
3	5	427.5	22.5	325	23.8	9.5	19.9	26.9		
4	20	360	90	310	16	8.5	17.5	22.1	1.6	2.6
5	20	360	90	360	23.2	6.4	11.3	16.4	2.6	4.5
B CEM II 32.5 R (3790 cm^2/g)										
6	0	450	0	310	21	6.5	18.9	25.8	4.6	6.2
7	5	427.5	22.5	310	19.3	6.7	17.9	22.8	3.7	5.7
8	5	427.5	22.5	325	21.3	5.8	16.3	21.3	3.9	5.8
9	20	360	90	310	14	5.2	11.7	14.4	2.3	3.8
10	20	360	90	360	20.7	3.5	7.3	11.0	3.6	5.6

Table 4.5 Effect of plasticizer on consistency (A CEM I 42.5 R)

	Plasticizer, %	Flow diameter, cm
1	-	17
2	0	15
3	0.3	15.5
4	0.6	17
5	0.75	17.5
6	0.9	18.5
7	1.2	18.5

Table 4.6 Effect of plasticizer on consistency (B CEM II 32.5 R)

	Plasticizer, %	Flow diameter, cm
1	-	17
2	0	14.5
3	0.3	15.5
4	0.6	17.5
5	0.9	18.5

Table 4.7 Effect of retarder on setting time, (A CEM I 42.5 R)

	Retarder, %	Initial set, h	Final set, h
1	-	3.5	4.6
2	0	2.8	3.7
3	0.05	3.5	4.5
4	0.06	3.6	4.8
5	0.07	3.7	4.7
6	0.08	3.9	5.0
7	0.09	4.1	5.1

Table 4.8 Effect of retarder on setting time (B CEM II 32.5 R)

	Retarder, %	Initial set, h	Final set, h
1	-	3.8	5.2
2	0	3.6	3.8
3	0.03	3.3	4.7
4	0.05	3.6	4.8
5	0.07	3.9	5.3
6	0.09	4.3	5.6

Table 4.9 Norm mortar experiments with four different cements that were substituted with waste at 5% ratio

	Cement type	Cem. (g)	Waste (g)	Retard. (%)	Init. set (h)	Final set (h)	1-day comp. str. (MPa)	7-day comp. str. (MPa)	28-day comp. str. (MPa)
1	A CEM I 42.5 R	450	-	-	1.6	3.1	28.0	36.9	51.1
2	A CEM I 42.5 R	427.5	22.5	-	1.6	2.9	29.3	39.1	49.8
3	A CEM I 42.5 R	427.5	22.5	0.05	1.8	2.8	32.2	45.2	50.9
4	A CEM II 42.5 N	450	-	-	2.2	3.3	31.6	44.0	53.4
5	A CEM II 42.5 N	427.5	22.5	-	1.0	2.5	33.3	45.5	49.6
6	A CEM II 42.5 N	427.5	22.5	0.05	2.2	3.1	33.3	49.8	52.9
7	B BPÇ 52.5 N-85	450	-	-	1	2	38.6	50.5	56.7
8	B BPÇ 52.5 N-85	427.5	22.5	-	0.6	1.7	37.4	48.4	54.1
9	B BPÇ 52.5 N-85	427.5	22.5	0.05	0.8	1.7	37.9	48.9	55.7
10	B CEM I 42.5 R	450	-	-	1.8	3.3	29.9	36.9	43.6
11	B CEM I 42.5 R	427.5	22.5	-	1.5	2.8	31.5	39.5	42.5
12	B CEM I 42.5 R	427.5	22.5	0.05	1.7	4	31.8	40.1	46.5

(1350 g of standard sand and 225 g of water was used; setting time was measured with scale used for the micro concrete)

Table 4.10 Results of activity index measurements of solid waste by using CEM I 42.5 R cements manufactured by two different producers

	28-days compression strength, MPa	
	A cement	B cement
Reference sample [1]	55.1	50.0
Sample with solid waste [2] (%75 cement + %25 waste)	40.8	38.6
Ratio [2/1] (%)	74	77

Table 4.11 Percent Cl^- and fineness values of the cements used in experiments

Cement	Cl^- (%)	Blaine (cm^2/g)	Bulk density (g/cm^3)
A CEM I 42.5 R	0.005	3790	3.11
B CEM II 42.5 R	0.003	4950	3.01
B CEM II 32.5 R	0.003	3790	2.93