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Resistance to Chlorides of the Alkali-Activated Slag Concrete

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This paper presents an analyze the role of chlorides in causing corrosion in the alkali-activated slag (AAS) concrete, its mechanism of action, the critical threshold on. Rapid Chloride Permeability test (RCPT) was conducted to measure the chloride permeability, relative permeability (RP) and the AC resistivity were measured on concrete AAS following the guidelines of ASTM C1202. The result was a contrast between a model of lifetime prediction that can be used to determine the chloride diffusion in concrete structures AAS and represents the influence of cementing AAS in the behavior of the chloride concentration on the surface of concrete, and data acquired with the techniques described above.

Keywords: Granulated blast-furnace slag, Portland concrete, compressive strength, permeable voids, absorption, chloride permeability.

1. INTRODUCTION

The activated slag concrete are a mixture of ground granulated slag, fine and coarse aggregates, and alkaline solution (sodium silicate) in the amount required for the concrete mix. This material is being studied by a number of researchers [1] as it has technological and economic advantages compared with Portland cement (OPC), for example, lower heat of hydration, low permeability, greater resistance to high temperatures, higher chemical resistance, elevated mechanical strength, among others. [2]

It has been determined that materials made from slag activated, regardless of type and concentration of the activator incorporated, have a capillary absorption coefficient lower than that reported for mixtures of OPC and therefore have been considered as materials with high resistance to capillary water penetration [3,4] providing them with a potential high resistance to acid corrosion. Referring to concrete made with Portland cement, certain mineral acids such as HCl, HNO_3 and H_2SO_4

can be very aggressive because the alkaline nature of the reaction products, leading to the complete destruction of the material [5,6] .

In activated slag concrete, it has been reported that the diffusion rates of the chloride ions are 30 to 40 times slower than in Portland cement mixtures at equal water / binder ratios, and additionally, It has been determined that the mechanisms are diffusion and capillary suction [7]. For transporting chloride ions through the concrete matrix is necessary that its structure is porous and has a certain continuity, ie to form suitable channels for which the chloride ions can move. These ions can be present in the fresh concrete mixture, dissolved in the aggregates, in the additives, or in water. The chloride ion can also penetrate further inside the concrete from the outside by diffusion. For reinforced concrete, the absorption of the salts set anodic and cathodic areas, the resulting electrolytic action leads to corrosion of the steel, with consequent rupture of concrete surrounding it. Chloride ion diffusion in the concrete is reduced by the capacity of the cement to combine it chemically or physically, as it reacts with the hydration products.

The aim of this paper is to implement a model of lifetime prediction for alkali activated slag concrete to predict the corrosion behavior of a structural steel embedded in alternatives concrete exposed to chlorides.

2. MATHEMATICAL MODELING OF CHLORIDE PENETRATION INTO CONCRETE

The diffusion in a porous medium such as concrete, is a phenomenon of chloride ion transport and is the principal mechanism for chloride penetration into concrete. Their study is based on obtaining three main parameters: the chloride concentration, the diffusion coefficient and the concentration of chlorides in the concrete surface. According to Fick's second law of diffusion, a one-dimensional transport process is assumed [8,9,10] (Eq. 1).

$$\frac{\partial C}{\partial t} = D_a \frac{\delta^2 C}{\delta x^2} \tag{1}$$

Assuming $C(x,0) = 0, C(0,t) = C_S$, and the diffusion coefficient constant D_a, analytical solution is obtained from equation 1 (Eq. 2) [8,10,11]

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{D_a t}}\right)\right] \therefore D_a = apparent\ diffusion\ coefficient \tag{2}$$

Where *x* is the depth of measurement given in millimeters, and *t* is the elapsed time in seconds. Although Equations 1 and 2 describe appropriately the behavior of the chloride concentration within the concrete structure, the assumption of having a constant diffusion coefficient D_a, limits the use of the equation. A model that can accurately estimate the profile of chloride penetration into the concrete during long term should incorporate a variable diffusion coefficient with time D_c [10,12].

Sagüés et al, determined a model to estimate the diffusion coefficient according to the time ($\frac{cm^2}{s}$), specifying its use to mixtures where the water/cement ratio lies on the range of 0.32 to 0.41 and cement´s amount between 390$\frac{kg}{m^3}$ and 446$\frac{kg}{m^3}$ (Eq. 3) [13,14,15].

$$D_{estimated} = 1.1 * 10^{-4} * F_1 * F_2 * \left(1 + \frac{\frac{w}{c} - 0.32}{0.09}\right) * \left(1 + \frac{446 - c}{56}\right) \quad (3)$$

Where F_1 is the additions' influence factor in the blend, F_2 is the age factor, the water/ cement ratio corresponds to the w/c proportion and the coefficient c is the cement´s amount expressed in $\frac{kg}{m^3}$. The factor F_1 varies in concordance with the used aggregates in the mixture (table 1) [13,14,15].

Table 1. Additions' influence factor in the blend

Aggregates		**F_1 value**
Type of aggregate	Concentration %	
Fly ash	18%-30%	1
Silica fume	8%-10%	
Slag	>70%	
Without any kind of aggregate		3

References [14,15] define the age factor F_2 as follows in the relation expressed on Equation 4.

$$F_2(t) = \left(\frac{t_0}{t}\right)^{\alpha} \quad (4)$$

Where t_0 is the reference time given in years and α is the ageing coefficient. References [14,15] parameterized equation 4, with a reference time of 1 year (Eq. 5).

$$F_2(t) = \left(\frac{1}{t}\right)^{-0.7} \quad (5)$$

Then the substitution of the equation 5 in equation 3 is possible using the table 1 relations (eq. 6).

$$D_a = 1.1 * 10^{-4} * \left(\frac{1}{t}\right)^{-0.7} * \left(1 + \frac{\frac{w}{c} - 0.32}{0.09}\right) * \left(1 + \frac{446 - c}{56}\right) \quad (6)$$

In the same way it is possible to substitute the equation 6 in the equation 2 to obtain the chlorides' penetration model for concrete with a concentration higher than the 70% of alkali activated slag, with water cement ratio between 0.32 and 0.41 with a cement content of 390$\frac{kg}{m^3}$ to 446$\frac{kg}{m^3}$. (Eq. 7).

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{t * 1.1 * 10^{-4} * \left(\frac{1}{11}\right)^{-0.7} * \left(1 + \frac{\frac{a}{c} - 0.32}{0.09}\right) * \left(1 + \frac{446 - c}{56}\right)}}\right)\right] \quad (7)$$

3. SAMPLES OF CONCRETE, PREPARATION OF SPECIMENS AND CARRYING OUT THE EXPERIMENT

To the corrosion study in these materials a concrete based on alkaline activated slag was used. The AAS blends employed granulated blast-furnace slag as cementing resource, table 2 shows the slag's composition, it was activated with sodium silicate ($Na_2\ O_3\ Si$) with a Na_2O concentration of 5% expressed as the incorporating slag weight percent, with a relation SiO_2/Na_2O of 2.4.

Table 2. Chemical composition of the slag.

Composition	Percentage by weight (%)
SiO_2	33.7
Al_2O_3	12.8
CaO	45.4
TiO_2	0.5
MgO	1.0
specific gravity [g/cm^3]	3.0

The concrete blend contained a cementing material dose of $400 kg/m^3$. It was assumed the ratios water/slag and activating compound/slag are equivalents, 0.5 ratio, in order to get an accurate concrete slump (70 to 100mm). The used aggregates correspond to a maximum size gravel of 19 mm, with specific gravity of $2940\frac{kg}{m^3}$, specific unit mass of $1860\frac{kg}{m^3}$, loose unit mass of $1700\frac{kg}{m^3}$, and 1.3% of absorption rate, compact sand with a specific surface of $2470\frac{kg}{m^3}$, compact unit mass of $1670\frac{kg}{m^3}$, loose unit mass of $1580\frac{kg}{m^3}$, and 2.9% absorption rate. Finally, for the activated slag's mixture curing it was conditioned a controlled environment, with relative humidity of 90% and a constant temperature of 20°C [8].

3.1 Tests for Concentration of Chlorides

In order of determining the concentration of chloride ions in the concrete and their penetration depth, tests that follow the ASTM C1543-02 norm were carried out on specimens which had been cured during 91 days. Cylindrical specimens with dimensions of 100 Ø ×120 mm were used in the process, during the experiment, specimens were plunged in distilled water with calcium hydroxide $Ca(OH)_2$ dissolved in it, the entire process was carried out inside a closed recipient. The specimens were kept until a constant weight was reached equals to a mass vary of ±0.1%, afterward the specimen was plunged for a period of 28 days in distilled water with sodium chloride (NaCl) dissolved in it. The solution had a constant concentration of 4% and remained unchanged during the length of the essay, even though necessary adjustments were done every week in order to guarantee the concentration levels [10].

Table 3. Physical characteristics, initial conditions, and measured penetration for samples based on activated slag under chloride attack

Sample type	Measuring depth (mm)	Sample concentration at 28 days (% by weight of cement)
AAS ($C_{o28\ days} = 4\%$)	0	3.98
	5	3.86
	10	3.52
	15	3.25
	20	2.92
	25	2.61
	30	2.34
	35	2.21
	40	2.01
	45	1.84
	50	1.65
	55	1.46
	60	1.14
	65	0.98
	70	0.88
	75	0.73
	80	0.64
	85	0.48
	90	0.42
	95	0.36
	100	0.3

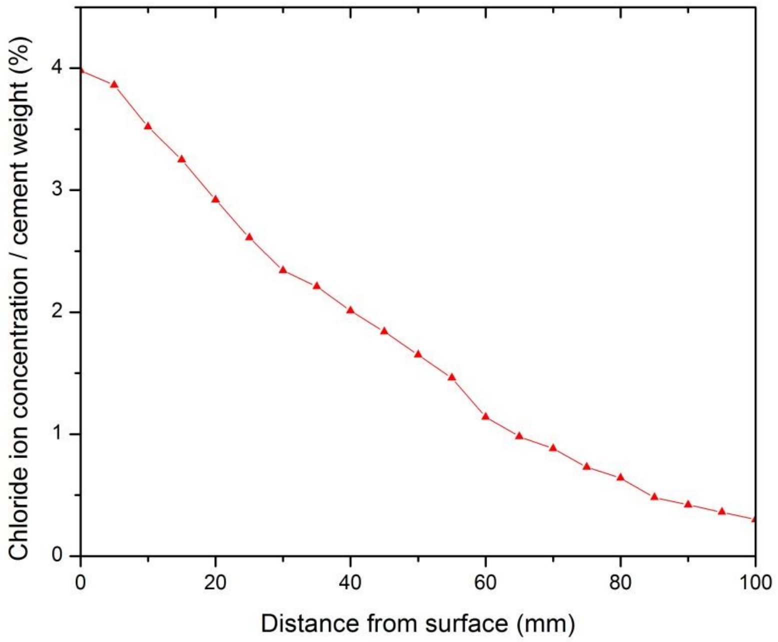

Figure 1. Chloride penetration profile (samples taken at 28 days)

At the end of a 28 days period, the specimens were withdrawn from the solution and the measurements were taken. Samples were extracted from the dried material reaching the 100mm deep, taking them at intervals of approximately 5 mm (Table 3) in order to describe the profile of penetration of chlorides (Fig. 1). Samples were extracted using a drill press.

3.2 Comparison between the measurements taken and mathematical model estimation

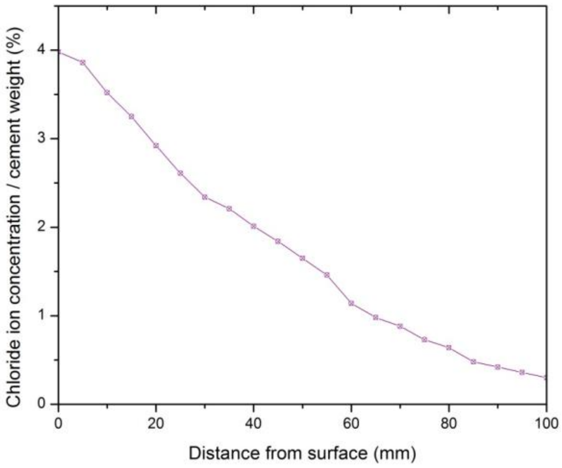

Figure 2. Chloride penetration profile (estimated mathematical model to 28 days)

Table 3. Comparison of the measurements

Sample type	Measuring depth (mm)	Sample concentration at 28 days (% by weight of cement)	Sample concentration at 28 days (Mathematical Model) (% by weight of cement)	Error %
AAS ($C_{o28dias} = 4\%$)	0	3.98	3.940822	0.99
	5	3.86	3.704516	4.19
	10	3.52	3.411559	3.17
	15	3.25	3.123592	4.04
	20	2.92	2.842952	2.71
	25	2.61	2.57179	1.48
	30	2.34	2.312029	1.2
	35	2.21	2.065317	7
	40	2.01	1.833003	9.65
	45	1.84	1.616117	13.85
	50	1.65	1.415368	16.57
	55	1.46	1.231143	18.58
	60	1.14	1.063529	7.19
	65	0.98	0.912332	7.41
	70	0.88	0.777111	13.23
	75	0.73	0.657212	11.07
	80	0.64	0.551808	15.98
	85	0.48	0.45994	4.36
	90	0.42	0.380554	10.36
	95	0.36	0.312541	15.18
	100	0.3	0.25477	17.75

Using the mathematical model, in which the parameters of the concrete specimens which had undergone the different tests were set (alkali activated slag content by weight of cement, water cement ratio, measuring distance and time), a theoretical chloride penetration profile was obtained (Fig. 2) which served as a base to contrast the measurement taken in an experimental way.

Table 3 indicates, that the average error gotten from all the specimens was 8.85%. The figure 3 shows graphically the comparison between the experimental profile (obtained from de AAS concrete specimen that had undergone a chloride's concentration of 4% for a period of 28 days) and the theoretical one obtained from the mathematical model.

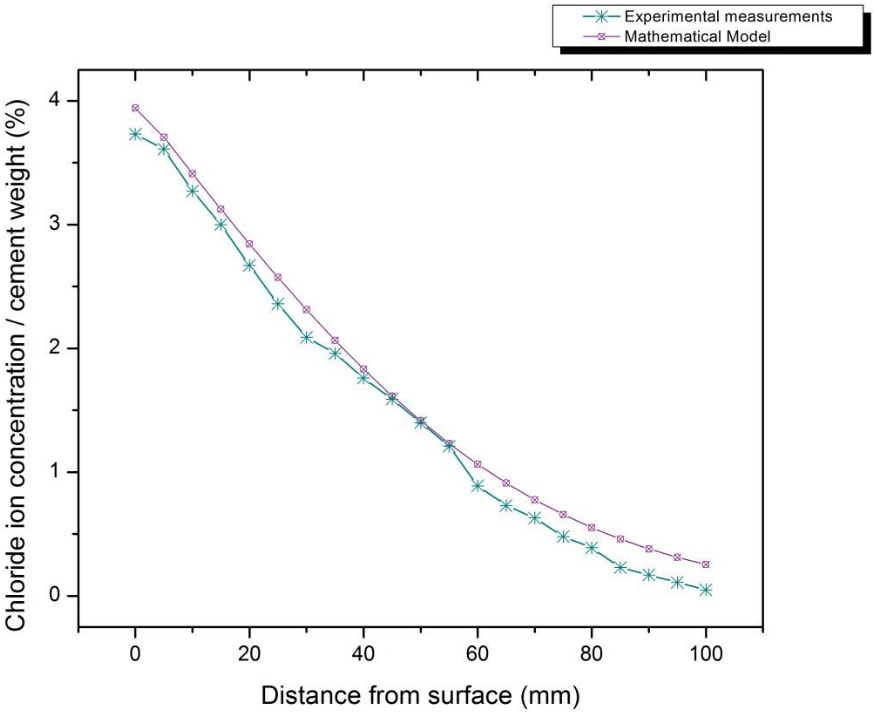

Figure 3. Comparison of chloride penetration profile obtained experimentally and theoretically by mathematical model in specimens tested at 28 days

4. ADDITIONAL TEST (ABSORPTION AND POROSITY), ON SPECIMENS UNDER CHLORIDE ATTACK

The absorption and porosity tests of the studied concretes were done over cylindrical samples with 76mm of diameter and 10mm of thickness following the process described in the ASTM C642 norm.

The resistance to chloride penetration of concrete with 28 days curing was determinated through permeability and penetration swift tests of chlorides. Cylinders with a diameter of 76.2 mm and 50 mm of thickness and exposed area of 60 mm^2 were used following the ASTM C1202-12 norm. The resistivity's values were gotten through the equation 8.

$$\rho = \frac{V \times A}{I \times L} \tag{8}$$

Where V = 60V, I is the initial current measured in amperes, L measured length in centimeters (50 cm) and A is the exposed area (cm^2).

Table 4 shows the behavior of the studied concrete depending on the transferred charge, this shows that the AAS concrete has low permeability.

Table 4. Chloride permeability of AAS concrete.

	Charge [Coulombs]	**Chloride Permeability**	**Initial Current [A]**	**Resistivity [kΩ-cm]**
AAS (28 days of curing)	1010.52	Low	0.0267	7.840

For concrete AAS, it is evidenced that after 28 days of evaluation, the concrete is classified as a very low permeability, therefore in this process there has been a pore clogging, these results are comparable with those reported by Shi Caijun (2000) [16].

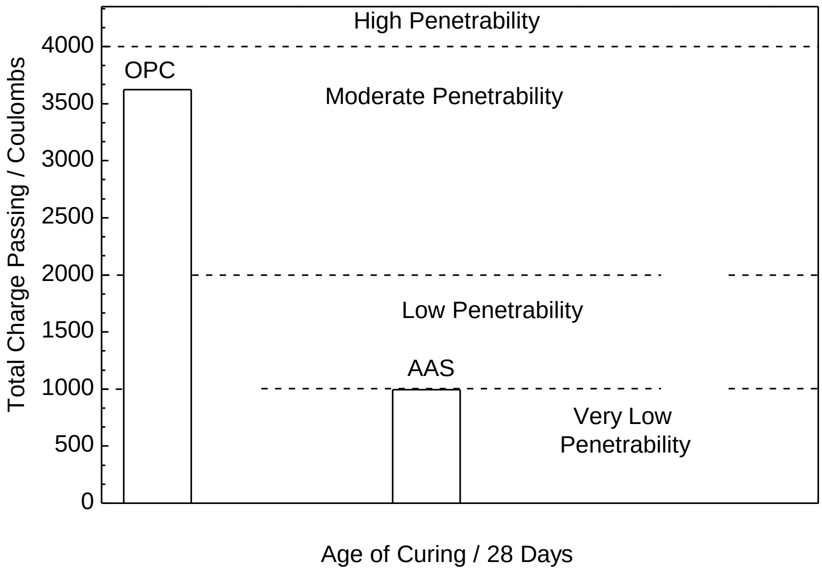

Figure 4. Values of permeability to chlorides in AAS concrete

Measuring the resistivity of concrete is used to interpret the value of the corrosion rate because it is intrinsically related to the moisture content of the concrete. Quick test chloride ion permeability (Fig. 4), is essentially a measure of electrical conductivity that depends on the pore structure and chemistry of the solution thereof. For a given size of the specimen and a voltage applied, the initial current recorded can be taken as representative of the electrical conductivity of the simple, it indicates that the chemistry of the pore solution appears to contribute more to the electrical conductivity or the charge passed to the pore structure. [16]

Resistivity values obtained can be seen in Table 4 and Figure 5, the tendency of the specific resistance for the AAS indicates that over time, the value of resistivity increases, Thus, the measurement of electrical conductivity depends on the pore structure and chemistry of the pore solution. For experimental conditions was taken into account that the starting current can be taken as representative of the electrical conductivity of the specimen.

A comparison was made between the total applied charge and the initial current creating a good linear correlation between the specimens. The slope of 55450 $\frac{C}{A}$ in Figure 5 is higher than 21600 $\frac{C}{A}$ theoretically expected (for a 6 hour experiment). This behavior can be attributed to an increase in temperature and the change in the structure occurred in the specimen during the experiment [17]. Some of these chlorides can react with the cement compounds, primarily tricalcium-aluminate (C_3A), chlorine ion forming stable. Excess of free chlorides leads to the initiation of the corrosion process.

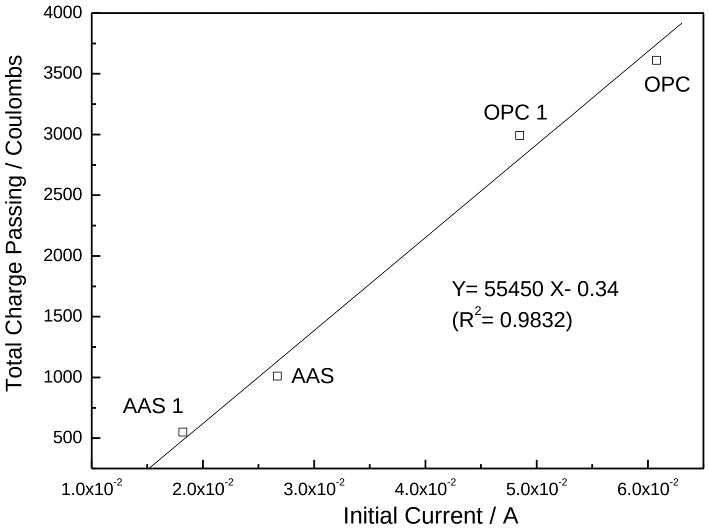

Figure 5. Relationship between the total charge applied and the initial current.

5. CONCLUSIONS

The proposed mathematical model of penetration of chlorides, based on the varying apparent diffusion coefficient allows, by entering characteristic parameters of the concrete composition (alkali activated slag content by weight of cement, water cement ratio) do the estimation of the concentration of chlorides through the interior of the structure. The great advantage is obtained when with the mathematical model, it is not necessary to perform a laboratory test on cores taken from the study site to determine the exact depths, but simply through an approximation to the characteristics parameters and performing variations on them, it can be determinated the behavior of the chloride penetration through the structure, avoiding to involve the study site.

AAS concretes exhibit a reduced value of chloride permeability. In general, this material can be considered as high performance. The electrical resistivity of these materials is high, suggesting the possibility of greater protection of steel in certain environments, specifically those where chlorides are present.

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