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Waste Materials in Construction: Putting Theory into Practice

THE LONG-TERM ACID NEUTRALIZING CAPACITY OF STEEL SLAG

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ABSTRACT. The long-term acid neutralizing capacity (ANC) of the electric arc furnace slag was investigated by batch pH titration, and the neutralizing processes of the slag were evaluated by reaction path modeling. Reaction time plays an important role for the determination of the ANC for the steel slag. The relatively slow reactions may give large contributions to the ANC for a long-term leaching process. pH-dependent reactivities of the steel slag were found in the high pH range. The neutralizing rates at high pH were much slower than that at relatively low pH. Below pH 9, the reaction rates became less pH-dependent and usually fast. The features of neutralizing reactions of the slag may be explained by its mineralogical composition and dissolution kinetics in the neutralizing processes.

1 INTRODUCTION

Steel slag is one of the important sources of industrial wastes. There is a long tradition in using the slag as potential secondary raw material in constructions and other fields. Recently more attention has been given the waste materials of environmental concern.[1] The possible environmental impact of the slag has to be investigated in order to assess whether the slag satisfies the requirements of a respective application, especially on the release of toxic elements in the leaching processes of the waste materials.

The pH environment of a given leaching system usually controls the dissolution of the waste matrix, and determines the release behaviors of many toxic elements.[2] The acid-base properties of solid wastes have been found to considerably influence the leaching of solid wastes by changing the pH environment. If a given aqueous system is well understood, the pH environment of the system can be defined by any two of these three parameters: (1) total dissolved acidic or alkaline substances, (2) the pH value of the system, and (3) the neutralizing capacity (acid neutralizing capacity (ANC) or base neutralizing capacity (BNC)).[3-4] Neutralizing capacity is, therefore, considered as one of the important acid-base properties of solid wastes. This capacity factor is significant for determining the shift of acid-base behavior of solid waste in leaching processes, and very useful for predicting the potentially reactive amount of solid waste in neutralizing reactions.

Many attempts have been made to assess acid-base properties of solid wastes including the neutralizing capacities.[5-8] However, how to define this factor is still an open question because of the complicated neutralizing reactions that take place during leaching. The central problem is that traditional test methods may only account for relatively fast reactions that take place in the initial leaching processes in the relatively short term. The long time reactivity of a solid waste must be considered. For long-term considerations, we must investigate the influence of reaction time on the determination of the neutralizing capacity, and define the importance of kinetic factors for the neutralizing reactions in leaching processes.

Many elements, minerals and even gas phases, as well as a wide pH range are involved in a heterogeneous waste system. Because of the complexity of the waste system, computer modeling should be one of the most useful approaches to give a good insight into the neutralizing processes. However, as current experimental methods do not take account of the long-term effect in the leaching test as mentioned above, most modeling work uses some simple geochemical models to find key factors that control the leaching behaviors of solid wastes.[9-15] In these models, thermodynamic equilibrium was assumed by which release of a species was determined by the solubility of a controlling mineral. The stability of the mineral was then connected with the pH environment. The knowledge of the key minerals that controlled the leaching environment became essential to understand the leaching processes. These models can not be used in dealing with reaction paths and kinetics. In some circumstances, the reaction path may become very important and kinetic factors may have a large influence on the leaching processes.

In addition, little work has so far been done to address the neutralizing capacity even for short-time leaching processes of steel slag. In this paper, we combine long-time experimental investigations with reaction path modeling to evaluate the neutralizing processes of the steel slag. Long-time experiments were used to investigate the time dependent neutralizing reactions, both short- and long-time neutralizing capacities and some kinetic information. The reaction path modeling was used to simulate the neutralizing processes. The simulations are performed over a pH range that may be interesting in the leaching of slag. The changes of solid phases and the chemical speciation in the aqueous phase were calculated in these simulations. The simulation results then were compared with experimental observations whereby a better understanding could be established for the complex neutralizing processes.

2 METHODOLOGY

2.1 Experiments

2.1.1 Material

The steel slag used in this study is a scrap metal based steel slag produced from the electric arc furnace process. The main chemical composition of the slag is shown in Table 1. The samples of slag were oven dried at 105 ± 1 °C to constant weight. In order to minimize the effects of diffusion in the particles, the slag was finely ground to particle sizes less than 0.160 mm.

TABLE 1. Major elements in the steel slag

Element	Ca	Mg	Na	K	Al	Fe	Mn	Ti	P	S	Si
(mmol/g)	5.51	1.86	0.02	0.01	0.81	4.33	0.72	0.06	0.15	0.04	2.05
(% by weight)	22.2	4.50	0.04	0.05	2.20	24.3	3.90	0.28	0.46	1300*	5.80

* The unit is ppm.

2.1.2 pH titration procedure and analysis of leachate

Long-term batch pH titration experiments were carried out for the steel slag by using the automatic titrator (Metrohm 719S Titrino). The slag sample was mixed with pure water in a liquid to solid ratio 5:1 (40 g ground slag and 200 ml of water) in a plastic bottle. HNO_3 solution (usually 1 M) was used as titrant. The acid was automatically added to keep a constant pH value (a given pH ± 0.02). The experiments were performed at different pH levels, and were run from 4000 to 6000 hours. The acid neutralizing capacities (ANC) of the steel slag were determined for different titration times and for various pH levels.

The leachates were analyzed after one week. The samples of leachate were taken from the batch experiments. The main cations, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) were determined by using the DIONEX DX-300 Series Ion Chromatography System with suppressed conductivity detection.

2.2 Modeling of the neutralizing processes

2.2.1 Modeling concept

The conceptual description and approach to conceive the solid waste-water reaction processes can be found in our previous work.[16-17] A reaction path model was used to simulate the pH titration process of the steel slag. The original theoretical approach was proposed by Helgeson et al.[18-20] to calculate a reaction path that involves one or more irreversible processes in which a series of successive partial equilibrium states may result in a state of local equilibrium for a reaction system. The basic idea used in the modeling of neutralizing reactions is to simulate the pH titration process as it is performed in the laboratory. A very small amount of slag is added to the water with known initial concentration. By using a geochemical reaction path model the rate of change of the water composition and the dissolution of the slag is calculated. The slag is modeled as consisting of its individual elements as found in the total analysis. The potential formation of secondary minerals is checked for from a list of many possible minerals the most supersaturated is precipitated first, then the next in line and so on. Some (more) acid and some more slag are then added and a new reaction path is calculated superimposed on the first. The procedure is repeated until all the interesting pH range has been covered. The whole titration process is considered as an irreversible process, but partial equilibria between solid phases and aqueous phase are assumed to exist.

2.2.2 Computer code

A geochemical computer code—EQ3/6 was employed to calculate the reaction path of the titration process.[21] In these calculations, solid waste and acid solution were treated as two special reactants. Relative reaction rates between solid waste and acid titrant were handled by a relative rate law,[22] and by defining the rate constants for these two special reactants respectively. An internal model is included for complex reactions and calculation of activity coefficients for the species in the aqueous phase. The main results of modeling are given in the distributions of species (including proton) in both solid and aqueous phases during the simulations, and equilibrium states of the reaction system along a certain reaction path.

2.2.3 Modeling system

For the modeling of the neutralizing reaction, the steel slag was represented by a four-component CaO-MgO-SiO_2-Al_2O_3 system. We also include oxides of sodium and potassium, as well as carbonate and sulfate, so that the original chemical composition of the slag could be represented. This is also reasonable for the mineralogical composition of steel slag.[23-24] In the reaction path modeling, these four components and relative reaction rates of steel slag were taken as main modeling parameters. Other minor constituents of the slag were usually considered to be less important for the neutralizing reactions. The system was assumed to be closed so that the interactions of the system with the atmosphere were ignored. In addition, the system was in an oxidative environment as the titrant was HNO_3.

According to the experimental leaching characteristics of the steel slag, only a part of the steel slag reacts in the neutralizing processes. The initial guess for the reactive fraction can be taken from special availability experiments of various components. The final reactive fraction of the slag will be obtained from the modeling by curve fitting in order to get the best agreement with the experimental results.

In the simulations, equilibrium was maintained among aqueous species and potential minerals. Although the computer code can automatically make optimum-choice from the database based on the phase rule, some adjustment was always required. The problem is related to the formation of the secondary minerals. Those that would form from purely thermodynamic consideration are often not minerals that are observed to form under similar conditions. Rarely are the secondary minerals determined or sought for in leached slags. We have therefore tested if the choice of secondary minerals is crucial. It has been found that an individual mineral is not crucial, although the mineral assemblage plays important role in the neutralizing reactions.[17] This can be understood considering that many of these minerals consist of the same building blocks, namely aluminum oxide, silicon oxide, calcium oxide and so on but in different proportions and with different cations. The choice of the secondary minerals is thus to some extent subjective but in most cases we have studied the simulated titration results are quite similar.

3 RESULTS AND DISCUSSION

3.1 Long-term acid neutralizing capacity of the steel slag

The experimental results for the long-term acid neutralizing capacities of the steel slag are shown in Figure 1. Two obvious features can be seen in this figure. One is that the changes of the ANC with time mainly appear in the experiments until about 500 hours. Another feature is that most of the acid neutralizing capacities are found in the pH range above 8.5. This means that there is a large buffering capacity in the relatively high pH range. It is less in the weakly alkaline or neutral pH range.

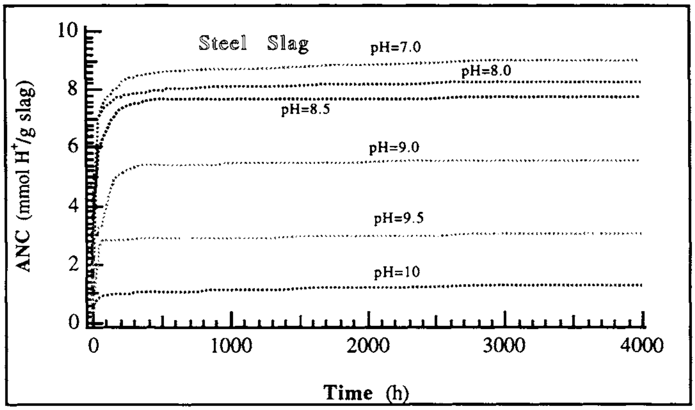

FIGURE 1. The acid neutralizing capacities (ANC) of the steel slag for different pH levels and reaction times.

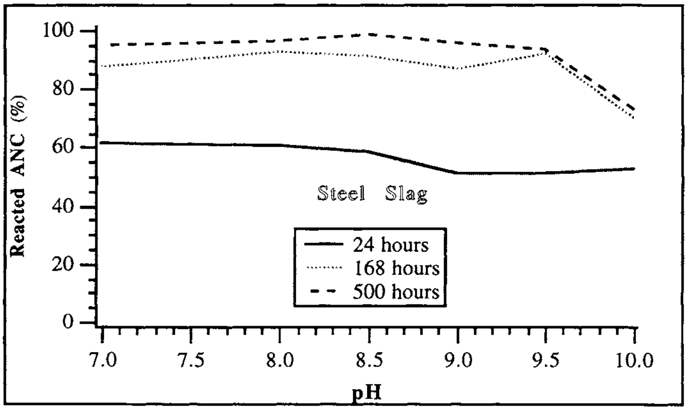

FIGURE 2. The amount of ANC needed as a function of the pH levels for different reaction times for the neutralizing of the steel slag

Because the acid neutralizing capacities for various pH levels only have very small changes after 4000 hours as shown in Figure 1, we may take these values as the approximately long-term neutralizing capacities of the steel slag. The relationships among the reaction time, the pH levels and the acid neutralizing capacities are shown in Figures 2 to 4. Figure 2 quantitatively indicates the importance of the titration time on the determination of the ANC. The 24-hour experiment only measured less than 60 percent of the long-term ANC for this kind of solid waste even using a sample which has very small particle size. If we wish to ensure that 95 percent of the long-term neutralizing capacities is obtained, the experiments need to run more than 500 hours for the pH range below 9. The experimental results for 24 hours, one week (168 hours) and 500 hours are shown in Figure 3. In order to evaluate the neutralizing processes of the slag, the pH titration curves for 24- and 168-hours were used to compare with the geochemical modeling for short time and relatively long time neutralizing processes since the 168-hour curve is close to that of the 500-hour.

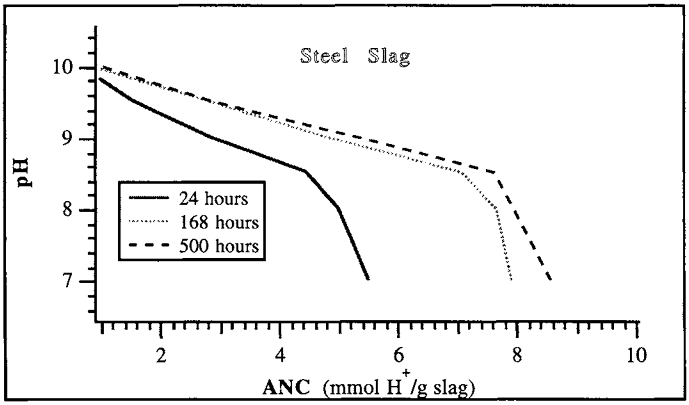

FIGURE 3. The pH levels as a function of the ANC for different reaction times for the neutralizing of the steel slag

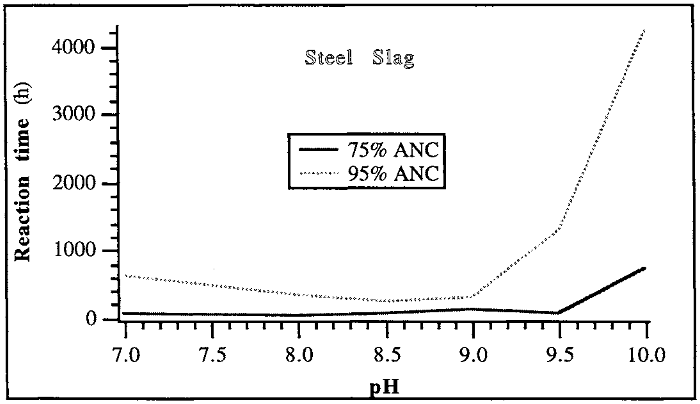

FIGURE 4. The reaction time as a function of the pH levels for different amounts of the ANC needed for the neutralizing of the steel slag

It was also found that the consumption rates of the ANC are pH dependent in the high pH range. Figure 4 provides the consumption times for 75 % and 95 % of the long-term ANC under different pH levels. The time needed to obtain the ANC increases considerably above pH 9. Thus the neutralizing reaction rates increase with decreasing pH in this range. Below pH 9, the reaction time becomes less pH dependent though the reaction rates were fast. These phenomena should be related to the mineralogy of the slag and kinetics of the neutralization reactions The detailed discussion will be given later.

3.2 Evaluation of the neutralizing processes

3.2.1 Simulations of the neutralizing processes

Two cases were studied by simulation of the neutralizing processes. One case is to simulate the 24-hours batch titration experiment (Case 1), and the other is the 168-hours experiment (Case 2). The final parameters used in the simulations are listed in Table 2, the reactive fractions of main elements are given in Table 3, and the potential secondary minerals which may precipitate are shown in Table 4. The simulation results are compared with the experimental data. The comparisons of pH titration curves for both short-term (24-hours) and relatively long-term (168-hours) experiments are presented in Figure 5. It is seen that a very good agreement between the modeling and the experiment has been obtained. Besides the proton, the distributions of other main cations in the aqueous phase were also compared with the simulations for different pH values (Figure 6). A general agreement between the simulations and the experiments has been obtained particularly for the most important cation, calcium in the 168-hour experiments. From these comparisons, it has been verified that the reaction path modeling works well in the simulation of neutralizing processes for the steel slag. The differences between the short and relatively long term neutralizing processes of the slag have also been distinguished by the modeling. This is clearly found from the final parameters of the simulations (Table 2 and 3).

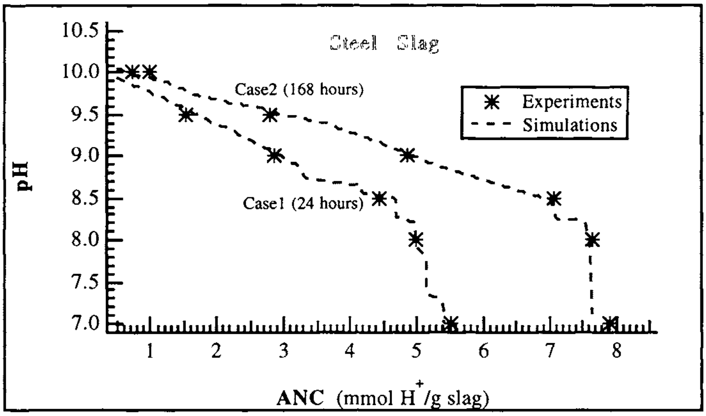

FIGURE 5. Simulations of the neutralizing processes of the steel slag

TABLE 2. Modeling parameters used in the simulations

	Reactive concentration of main components of the slag (mmol/g)							The ratio of
	CaO*	MgO*	Al_2O_3*	SiO_2*	$CaCO_3$	Na_2SO_4	K_2SO_4	rate constant**
Case 1	2.745	0.056	0.004	0.021	0.01	0.003	0.001	0.8000 - 0.9029
Case 2	3.572	0.336	0.012	0.105	0.01	0.008	0.004	0.6250 - 0.6925

Case 1 means the 24-hours batch titration experiment, and case 2 the 168-hours experiment.

* Major modeling parameters including the ratio of rate constant. The others usualy keep constant.

** The ratio of rate constant of dissolutuion of slag to the acid addition

TABLE 3. Reactive fractions of main elements in the neutralizing processes

	Ca	Mg	Na	K	Al	Si	S
Case 1	0.50	0.03	0.30	0.20	0.01	0.01	0.10
Case 2	0.65	0.18	0.80	0.80	0.03	0.05	0.30

Case 1 means the 24-hours batch titration experiment, and case 2 the 168-hours experiment.

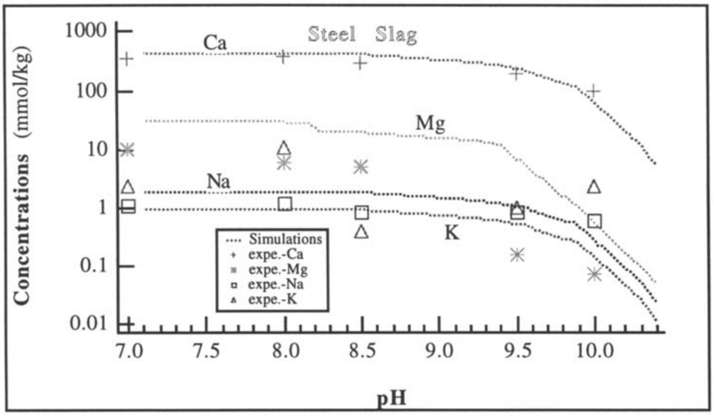

FIGURE 6. Comparison of simulation with experiments for dissolved species in aqueous phase during the titration of steel slag for 168-hour experiments

TABLE 4. Potential secondary minerals that appeared in the simulations

Minerals	Formulas*
Brucite	$Mg(OH)_2$
Calcite	$CaCO_3$
Chrysotile	$Mg_3Si_2O_5(OH)_4$
Clinochlore-14A	$Mg_5Al_2Si_3O_{10}(OH)_8$
Dolomite-ord	$CaMg(CO_3)_2$
Gibbsite	$Al(OH)_3$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Mesolite	$Na_{0.676}Ca_{0.657}Al_{1.99}Si_{3.01}O_{10} \cdot 2.647H_2O$
Montmor-Ca	$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$
Saponite-Ca	$Ca_{0.165}Mg_3Al_{0.33}Si_{3.67}O_{10}(OH)_2$

* Based on EQ3/6 Thermodynamic Database (GEMBOCHS. V2-EQ6-DATA0•COM•R2, 1995-09-02)

3.2.2 Characteristics of the neutralizing processes of the slag

The final parameters of the geochemical simulations (Table 2) indicate which component of the slag plays an important role in the neutralizing processes. It is obvious that Ca-, Mg- and Si-containing minerals are important for the neutralizing reactions. The calcium component provided the largest amount of acid neutralizing capacity in the titration. It should be noted that the carbonation seems to have no large influence on the ANC because the buffer capacity is small below pH 8.5.

The differences between the long- and short-time neutralizing reactions appeared mainly in the reactive fraction of the slag and the reaction rate. Compared with short-time titration processes, the reactive fraction in a long-time titration process showed much larger increase in Si and Al than other elements. These elements are usually considered as main elements of the slag matrix. This indicates that matrix dissolution resulted in the difference between the long and short time titration processes. This feature can also be found from the ratio of reaction rate of slag to the acid addition. These ratios can be considered as the relative reaction rates of the slag in the neutralizing processes. From Table 2, it is found that the faster reaction rates corresponded to the short-time processes, and the slower rates exhibited in the long-time processes. This means that the short time titration experiments take account of the relatively fast reactions though the reactive fraction of the slag is smaller.

Mineralogy and dissolution kinetics of the slag considerably affect the neutralizing processes and the ANC. The major mineral phases of the electric arc steel slag may include calcium-silicate (dicalciumsilicate, tricalciumsilicate and dicalciumferrite), calciowustite, magnesiowustite, calcium aluminate, free lime and periclase.[23, 25] The hydration of the mineral phases is important for the neutralizing processes. The main reactions of the hydration are:[25]
for free-CaO and free-MgO,

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \tag{2}$$

for calcium silicates and calcium aluminate,

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO \bullet 2SiO_2 \bullet 3H_2O + Ca(OH)_2 \tag{3}$$

$$2Ca_3SiO_5 + 6H_2O \rightarrow 3CaO \bullet 2SiO_2 \bullet 3H_2O + 3Ca(OH)_2 \tag{4}$$

$$CaO \bullet 7Al_2O_3 + 12H_2O \rightarrow CaO \bullet Al_2O_3 \bullet 6H_2O + 6Al_2O_3 \bullet H_2O \tag{5}$$

According to the experimental results (Figure 4), both hydration reaction equilibrium and kinetics may have influence on the neutralizing processes of the steel slag. Hydration reactions of free-CaO and free MgO should result in a high pH value in the aqueous phase. These reactions may be fast and easily reach an equilibrium. However, some of the neutralizing reactions may be controlled by kinetic factors. In the relatively high pH range, the reaction time for certain ANC is reduced with the decrease of pH and the reaction rates are slow in comparison to those at lower pH. On the other hand, the hydration reactions appeared to be less sensitive to the proton and fast in the relatively low pH range. The pH-dependent reaction behavior of the slag may be attributed to the dissolution kinetics of the matrix minerals of the slag because this behavior more easily can be found from the long time experiments than from the short time experiments. It is obvious that the kinetic behavior of the slag is different from that of aluminosilicate minerals and silicate glasses. For normal silicate minerals and glasses, the dissolution rates are usually fast in both high and low pH ranges, and are slow in a neutral pH range.[26-27] Because the kinetic behaviors of the main mineral phases of the slag are not available, further assessment of the dissolution of the slag matrix will require more detailed empirical knowledge of these processes.

A general agreement between the simulations and experimental measurements in the distributions of the main cations in the aqueous solution (Figure 6) indicates that the assumption of local equilibria among the aqueous species and secondary minerals is reasonable for the relatively long-term neutralizing processes of the slag. The local equilibria may also result in that the neutralizing reaction rates became very low, because the dissolution of main mineral phases of the slag should be inhibited by affinity effect when saturation state of solution increases just as in a long time experiments. However, if the mechanisms of the neutralizing reactions or the reaction system are changed, the local equilibria will not be upheld, and the ANC of the slag could be different in a changed situation. For example, the ANC of the slag may be different if the neutralizing reactions are carried out in a flow-though system. We therefore need to consider the changes of reaction mechanisms and reaction system in order to have a comprehensive understanding for the neutralizing processes of the steel slag especially for a long-term consideration.

4 CONCLUSIONS

The determination of acid neutralizing capacity of the electric arc steel slag depends on reaction time. A short-time titration experiment may lead to a large underestimate of the ANC, particularly at low pH. About 500-hours experiment may be needed to account for about 95% of the ANC for the most interesting pH range.

The acid neutralizing capacities of the steel slag are different for different pH levels. Most of the capacities will be consumed in a relatively high pH range (above pH 8.5). In a low pH range, the slag may only provide limited ANC for neutralizing reactions in the time scale of thousands of hours.

The major contribution for the ANC comes from the Ca- (and Mg-) containing constituents of the slag. Comparison of long-time neutralizing process with the short-time one, the differences are in the reactive fraction of the elements and average reaction rates of the slag. For a long-time process, there were larger reactive fractions in Si and Al elements and smaller average reaction rates to account for dissolution of the slag, than that for a short-time process. The pH dependence of the ANC may be explained by the hydration reactions of main mineral phases and dissolution kinetics of the slag matrix.

The geochemical modeling works well in the evaluation of long-term ANC for the steel slag. It provides valuable information about the neutralizing reactions in both mineral and aqueous phases in this reaction system, which otherwise may not be easy to obtain from experiments.

The contribution to the ANC of Si and Al increases considerably with time. It is probable that the aluminosilicate minerals can give an additional significant ANC for very long times, i. e., in exess of 10's of years, this would give additional ANC in the near neutral range.

Acknowledgments

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