Original

Utilization of Slag Fibers as Ecomaterial

I . Characterization, Dissolution and Interfacial Properties in Aqueous Media

by

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ABSTRACT

A physical and chemical characterization to the slag fibers was carried out by several instrumental techniques. Its main components were Si, Mg and Al oxides. The distribution of these elements was constants and uniform in all slag fibers' body by its amorphous structure, which generates surface'sites with both positive and negative charges in aqueous solution, which is depending on the compound lacated in the site.

The dissolution behavior of the slag fibers was negligible in a wide range of pH (4 to 10) and temperature (25 to 95°C), which was an important collecting feature as ecomaterial. The slag fibers' dissolution at low and high pH was concordant with thermodynamic predictions. The differential dissolution by different elements of slag fibers produces a remarkably high difference between the point of zero charge (pH10.8) and isoelectric point (pH2.9) of this material.

Key Words : Slag Fibers, Ecomaterial, Dissolution, Isoelectric Point, Point of Zero Charge.

1. INTRODUCTION

The constant and increasing necessity to decrease the contamination levels produced by industrial waste water streams (reflected in new and more rigorous governmental regulations (1) and activities of environmentalist groups) and the decrease in natural resources compel that part of the research work orients its efforts in searching for alternative safe materials, new processes and waste reduction techniques such as recycling (2).

The use of slag, from several smelting processes, has increased considerably in the last few years, specially in the construction field. A brief review shows that the slag is used mainly as aggregates in

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paving to prevent cracking (3) and increase water permeability (4). As aggregate of refractory cement for increase in the thermal shock resistance (5). In the manufacture of high strength hardened products (6), boards (7–9), slag-alkaline binders (10), low density porous fillers (11), lightweight molded products (12) and lime-slag cement (13). As activator of binders (14). As aggregate in mortars to increase strength (15), density (16) and to use as coating for pipes and fittings (17). As aggregate in concrete to increase permeability and mechanical properties (18, 19) and to build walls (20).

The slag is also used in the decontamination field, which is being used in the removal of metal ions and cyanide (21, 22) in waste water treatment as biocarrier (23) and in aeration settling reactors (24).

In this research work this solid waste material, slag from a nickel electrorefining process, is employed as ecomaterial. By ecomaterial we shall understand a material capable of defending the environment against pollutant materials. The slag fibers are obtained by high speed spinning technique after smelting process. The slag fibers show very high efficiency as a collector of both organic and inorganic ultrafine particles (UHP) from low concentrated suspensions (25), by using as a collector bed system.

An ecomaterial, which will be used in a process such as waste water or waste stream cleaning, should have high feature to work in polluted systems and not harmful to the environment during its use. Thus, its behavior in aqueous media should be thoroughly studied.

The objective of this work was to characterize the slag fibers by measuring: 1) physical properties such as shape, size, composition and specific surface area, 2) chemical properties obtained from its dissolution behavior in aqueous media and 3) interfacial properties obtained from surface potential determinations. Knowledge of these properties is useful for effective processes for using the slag fibers as ecomaterial.

2. MATERIALS AND METHODS

The slag fibers (SF) used in this research work were obtained from Pacific Metals Co. All chemicals were analytical reagent grade obtained from Wako Pure Chemical Ind., and were employed without further purification. All aqueous solutions were prepared with double distilled water. All chemical analyses were performed by using inductively coupled plasma-emission spectrometry (ICP).

2. 1. Physical and Chemical Characterization of SF: This was performed with several instrumental techniques. Scanning electron microscope (SEM) to obtain shape and size, conventional microscope to procure its length, which were used to obtain its geometrical specific surface area. X-ray fluorescence (XRF) and diffraction (XRD) to get its composition and crystallinity. Electron probes x-ray micro analysis, mode energy dispersive x-ray spectroscopy (EPMA-EDX) to determine its elements' distribution. BET by nitrogen adsorption method to evaluate the real specific surface area of the SF. In all the analyses performed, standard procedures were followed.

2. 2. Dissolution of SF: This was performed to obtain the effect of the pH, temperature, electrolyte concentration and time in the SF's dissolution behavior. The experiments were carried out in glass containers where one gram of SF was immersed in 0.1 [dm³] of air-saturated aqueous KNO₃ solutions at different concentrations (0, 10⁻⁴, 10⁻³, 10⁻², 10⁻¹ and 1 [mol dm⁻³]). The effect of pH was evaluated in a range of 2 to 12; drops of HNO₃ and KOH were employed to adjust it. The experiments were conducted in a thermostatic bath to maintain the temperature of the solutions, which was fixed at 25, 50, 75 and 95°C; the glass containers were inside it. The experiments were performed without agitation

because when using the SF as collector of UFP is employed with the column bed system, where mainly hydrodynamic forces act. The trial time employed was 75 minutes. Samples of the liquid phase, approximately $0.015 \text{ [dm}^3\text{]}$, were obtained at several intervals of time. Before measuring the pH and concentration of Si, Mg, Ca, Al, and Fe, the samples were filtered with a filter paper ($4 \text{ [}\mu\text{m]}$ of pore diameter) to completely remove undissolved particles or fibers unfastened from the SF. Moreover, this filtraion was tested by centrifugation (18 [krpm] by 30minutes) and micro-filtration ($0.2 \text{ [}\mu\text{m]}$ of pore diameter). The results did not show any significant discrepancies concerning the first filtration. Therefore, only filter paper was used.

2. 3. Interfacial Properties of SF : These evaluations were performed to evaluate the surface potential, point of zero charge (PZC) and isoelectric point (IEP), of the SF as fibers and as particles by microtitration and electrokinetic measurements, respectively.

Particles of SF were obtained by dry milling a given quantity of SF in a ball mill during 24hours. The particles used in the evaluation of the point of zero charge (PZC) were classified 100% under mesh 325 Tyler ($44 \text{ [}\mu\text{m}]$). The particles used in the ζ -potential evaluation were obtained from a supernatant solution produced with SF ground by 30 minutes stirring and 30 minutes ultrasonifying followed by sedimentation in $\text{KNO}_3 \text{ } 10^{-2}$ and $10^{-3} \text{ [mol dm}^{-3}\text{]}$ solution for 10 days ; drops of KOH and $\text{HNO}_3 \text{ } 10^{-2} \text{ [mol dm}^{-3}\text{]}$ were employed to adjust the sol's pH.

The PZC of SF, as particles and fibers, was evaluated by the ion adsorption method using automatic microtitration with $\text{KOH } 10^{-1} \text{ [mol dm}^{-3}\text{]}$ as titrant agent. The ζ -potential of the SF, as particles, was evaluated by the electrophoresis method using a light scattering spectrophotometer. The ζ -potential of SF, as fibers, was evaluated by the streaming potential method using nitrogen gas.

3. RESULTS AND DISCUSSION

3. 1. Physical and Chemical Characterization : Electron micrographs show that the shape of the SF is as perfect cylinders. The real mean diameter of the SF was $5.60 < \phi < 6.12 \text{ [}\mu\text{m}]$, considering a 95% as a confidence interval by using "t" distribution. The SF's average length was approximately 4 [mm] . These data were used in the geometrical computation of the specific surface area (SSA) of the SF. The value found was approximately $0.23 \text{ [m}^2\text{g}^{-1}\text{]}$. The SSA of SF was computed in approximately $0.80 \text{ [m}^2\text{g}^{-1}\text{]}$ by using the BET method.

Both XRD and EPMA-EDX analysis showed that the SF was completely amorphous. It seems that there is not a cristallization effect during the SF production process.

Table 1 shows the composition of SF analyzed by XRF. The main components of the SF are SiO_2 , MgO and Al_2O_3 , which represent over 91% of its weight. It is important to indicate that complex oxides are also expected to be present in the SF structure, but were not determined in this work. Spot analysis made by EPMA-EDX to the surface and to the cross section of SF established that $\text{SiO}_2 : \text{MgO} : \text{Al}_2\text{O}_3$ ratio is $2.54 : 1.35 : 1.00$ and $2.58 : 1.32 : 1.00$ in its surface and in its inner part, respectively. The negligible variation among these ratios indicates that during the SF production process there is no preferential diffusion of elements. The distribution of the main elements in the SF is constant, uniform and homogeneous.

3. 2. Dissolution : Due to the origin of the SF, it should be considered as a complex process involving many different reaction steps and pathways. Different sites in its structure separately react with the solution and simultaneously undergo hydration, hydrolysis, ion exchange or condensation reactions.

Each of these reactions affects, and is affected, by the chemistry and the structure of the near surface region of the solid, as has been indicated by Casey and Bunker (26). On the other hand, the difficulty associated with the determination of the identity and stability of different species in solution from complex solids, is well known. This situation is not exclusively associated to this kind of compounds but also to simple oxides and their ions in solution (27).

In order to avoid the uncertainty that could appear during the analysis of the results, the dissolution data of the SF are interpreted if the total concentration of a given element, M, in solution is represented by the following expression :

$$M_T = \sum M_{(M_xO_y)_i} = \sum M_{(M_x[OH]_y(xn-y))_i} \quad [1]$$

where $M_{(M_xO_y)_i}$ represents the contribution to M_T of each oxide compound that has dissolved from the surface of the SF. More precisely, it represents the contribution due to the dissolution of different sites on the SF surface. $M_{(M_x[OH]_y(xn-y))_i}$ represents the contribution to M_T of each ion present in the liquid phase.

Fig. 1 summarizes the global dissolution behavior of SF in solution of $KNO_3 \cdot 10^{-3}$ [mol dm⁻³] at various temperatures. The results are given as global dissolution of SF, which is initial pH and experi-

Fig. 1 Global dissolution [ppm] behavior of SF in $KNO_3 \cdot 10^{-3}$ [mol dm⁻³] solution as a function of initial pH and experimental time. (a) 25°C, (b) 50°C, (c) 75°C and (d) 95°C.

mental time. The concentration of each element, obtained by eq. 1, in solution at 75 minutes is given in detail in Table 2. Fig. 1 shows that the global dissolution increases with temperature and occurs preferentially at extreme condition of acidity (pH 2). However, the dissolution is negligible within a neutral range of pH (approximately 4 to 10); independent of the temperature used. At extreme conditions of alkalinity (pH12), the total dissolution is less than 3% of the value found at pH 2 at 50,

Table 1 Composition of the Slag Fibers obtained by x-ray fluorescence analysis(XRF)

Compounds	SiO ₂	MgO	Al ₂ O ₃	CaO	Fe ₂ O ₃	Na ₂ O	TiO ₂	MnO	K ₂ O	P ₂ O ₅	LOI
[wt %]	48.37	24.31	19.18	1.240	1.580	0.630	0.430	0.330	0.265	0.024	3.66

Table 2 Concentration of the elements in solution [ppm], computed by Eq. 1, at 75 minutes in KNO₃·10⁻³ [mol dm⁻³] solutions at different pH and temperatures.

M _T	Temp.	Initial p H							
	C	2	3	4	6	8	10	11	12
Si _T	25	1.8550	1.5510	0.1797	0.1623	0.1735	0.2550	0.8740	1.1150
	50	193.00	12.300	0.9500	0.7500	0.7400	1.2000	2.2000	9.3000
	75	310.90	18.110	1.0960	2.5380	2.7100	4.0240	6.1910	19.880
	95	502.00	29.500	1.6940	7.0980	9.1640	8.3160	16.040	41.970
Mg _T	25	2.0010	1.8330	0.2123	0.0294	0.0264	0.0153	0.0000	0.0000
	50	55.000	14.500	1.3870	1.3270	0.2400	0.0800	0.0200	0.0000
	75	262.30	19.840	2.2500	1.4500	1.1350	0.9556	0.0400	0.0108
	95	414.50	28.390	2.2880	3.2380	3.3310	1.4120	0.3330	0.0128
Al _T	25	1.2640	1.1160	0.0200	0.0000	0.000	0.0000	0.0000	0.0000
	50	50.000	4.200	0.0715	0.0000	0.000	0.0000	0.3000	1.5000
	75	169.60	11.860	0.0845	0.4143	0.6768	0.3000	1.4420	2.2690
	95	292.40	16.220	0.4700	1.4860	1.9010	1.9100	1.9100	4.7340
Ca _T	25	0.4678	0.3165	0.1734	0.1308	0.1288	0.0666	0.0486	0.0260
	50	10.000	1.3970	0.4360	0.2273	0.2003	0.1524	0.1326	0.0500
	75	16.220	1.7500	0.4415	0.6150	0.5400	0.3500	0.1500	0.1000
	95	33.410	2.5820	0.8500	1.0920	0.6241	0.2391	0.2391	0.2127
Fe _T	25	0.1567	0.1220	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000
	50	0.2100	0.1490	0.0887	0.0000	0.0000	0.0000	0.0000	0.0000
	75	6.0000	0.7500	0.1500	0.0000	0.0000	0.0000	0.0000	0.0000
	95	20.970	2.1070	0.2657	0.0000	0.0000	0.0000	0.0000	0.0000

75 and 95°C. The same behavior described by Fig. 1 was observed when different electrolyte concentrations were used. Therefore, it appears that the electrolyte concentrations were used. Therefore, it appears that the electrolyte concentration has no influence on the dissolution phenomena.

As seen in Table 2, at extreme condition of acidity, the contribution to the global dissolution is given mainly by Si_T , Mg_T and Al_T , and in less proportion by Ca_T and Fe_T , which is attributed to their low content in the SF. This table also shows that at extreme condition of alkalinity (pH 12) approximately 90% of the dissolution correspond to Si_T , the rest to Al_T and Ca_T . The presence of Mg_T is negligible.

The results presented in Fig. 1 and Table 2 are consistent with thermodynamic predictions, which indicate that the dissolution of oxides, like those present in the SF, is favored at low pH. The potential-pH diagrams of the predominant oxides present in the SF; MgO , Al_2O_3 , CaO , Fe_2O_3 show that their dissolution will occur mainly in acidic conditions (27-28). At extreme condition of acidity (pH 2-3) only the more simple cations, M^{+n} , are expected in the solution phase. On the other hand, the negligible dissolution showed by the SF at neutral values of pH is explained due to the well known intrinsic stability of the oxides in this range of pH, especially in solutions of simple acids and bases (29).

Thermodynamically, at high values of pH (above 10) the existence of calcium ions is not favored. The presence of Ca_T should be attributed to $\text{CaCO}_3(\text{aq})$ that is formed from the atmospheric CO_2 dissolved in the solution phase. Based on the Henry's constant reported by Butler (30), the $\text{CO}_2(\text{aq})$ in solution was computed in approximately $10^{-5} [\text{mol dm}^{-3}]$, and was assumed constant in all range of pH. Computations based on the $\text{CO}_2(\text{aq})$ concentration, carbonic acid ionization constants, CaCO_3 stability constant and Ca_T in solution; established that CaCO_3 will be generated above pH 10.

The Al_T in solution (specially above 50°C) can be attributed to AlO^{-2} ion as indicated by Pourbaix (28), and/or by $\text{Al}(\text{OH})^{+2}$ ion as indicated by Våland and Heusler (31). The aluminum ion that could be present in solution under this condition is still a matter of discussion as pointed-out by Blesa et al. (29); nevertheless, its presence is a widely accepted fact.

Table 2 shows that the silica present in the SF preferentially dissolves at extreme condition of acidity (pH 2). Minimum dissolution occurs at a neutral range of pH. At extreme alkalinity (pH 12), Si_T in solution reaches only approximately 5%, 6% and 8% of its value of the other extreme of the pH range when the system was at 50, 75 and 95°C, respectively. This silica's dissolution behavior doesn't agree with most other studies of this oxide, which indicate that dissolution occurs preferentially at high pH (32). Iler (33) indicates that the dissolution of amorphous silica is not a simple matter of molecular transfer of $\text{Si}(\text{OH})_4$, the soluble form of silica, but there is also a chemical hydration-dehydration equilibrium. This reaction is catalyzed by hydroxyl ions as represented by the following reaction (33):

This reaction is indicating that the dissolution of silica will increase with the pH. Moreover, the monomer, in the presence of hydroxyl ions, is forming different polymers such as $\text{Si}(\text{OH})_5^-$ and/or HSiO_3^- . Nevertheless, it is important to indicate that the solubility of amorphous silica is still an uncertain matter. It depends on several factors such as particle size, genesis of the samples, presence of

impurities, and others. Van Lier (34) in its earlier work concluded that the solubility of silica varies considerably between different samples due to their chemical and structural differences. The dissolution of silica present in the SF can not be fully explained by the traditional form, which is based on the behavior of silica oxide containing some impurities. A more global focus is required, which includes the effect of the other oxides' dissolution and the change produced in the surface of the SF by this dissolution.

As was indicated in section 3.1 the SF is completely amorphous and its constitutive components are homogeneously distributed. Therefore, its surface must have different sites where the different elements are distributed. These sites will have both positive and negative charges, which will depend on the element located in the site, e.g., Mg, Al and Ca produce sites with positive charge, while Si produces the site with negative charge.

The surface' sites distribution could be explained by overlapping atomic layers with different structural elements. When these layers are in contact with solution at very low pH, say pH 2-3, elements such as Mg, Al, Ca and Fe quickly pass to solution producing a leached plane of high porosity in adjacent layers of the solid-liquid interface. This favors further deeper attacks on the solid phase, in a similar way as described by Casey and Bunker (26) for feldspar, and Hellman et al. (35) for albite. Under this condition, it could be expected that the silicon-oxygen and silicon-metal bonds become increasingly weak. With this increasing weakness, the bonds will break down producing the pass of Si_T into solution. In other words, the dissolution of the elements which "cover" or link the silicon's complex structure, produces the structure's instability and further favors its dissolution, as suggested by Table 2. On the other hand, at very high pH this situation is reverted. Those elements are almost not dissolved under this condition, that is, they remain in their locations. The Si_T that has dissolved from first layers of the SF will produce a leached plane of low porosity that will reduce the rate of contact between hydroxyl ions and silicon complexes. Consequently, the Si_T in solution phase at high pH is expected to be small in comparison with the value found at low pH.

The precipitation onto the SF surface of Mg, Al and Ca compounds may produce the same effect of "covering" the silicon complex sites of the first layers of SF as described above. Nevertheless, analysis made by SEM and EPMA-EDX to the SF surface after dissolution has not given results that can validate this assumption.

3. 3. Interfacial Properties : Fig. 2 shows the ion adsorption curves, which are indicated as the pH of HNO_3 10^{-3} [mol dm $^{-3}$] solution without SF, with 1 [g] of SF as fibers and with 1 [g] of SF as particles as a function of KOH 10^{-1} [mol dm $^{-3}$] solution spent during the titration. The point of zero charge (PZC) of SF was found approximately at pH 10.8 as the intersection point between the three curves indicated. As the PZC is 10.8 is expected that the SF surface be positive in a wide range of pH (<10.8). The isoelectric point (IEP) of SF was found approximately at pH 2.9 as seen in Fig. 3, a plot of ζ -potential [mV] as a function of KNO_3 10^{-2} and 10^{-3} [mol dm $^{-3}$] solutions' pH, used as supporting electrolyte. As the IEP is 2.9 is expected that the SF' surface be negative over this pH.

For a given material the PZC and IEP are expected to be equal, or at least close, when are measured by these two methods when H^+ and OH^- are the potential or charge determinant ions. The different values of PZC and IEP are attributed to the fact that the electrokinetic measurements are based on the movement of the particles suspended in a media (electro-phoresis) or on the media that is surrounding them (electroosmosis) when an electric field exists. Both measurements do not take into account the

Fig. 2 Ion adsorption curves showing the point of zero charge (PZC) of SF at 25°C. Where (a), (b) and (c) represent HNO_3 10^{-3} [mol dm^{-3}] solutions without SF, with 1 [g] of SF as fibers and with 1 [g] of SF as particles, respectively.

Fig. 3 Electrophoresis curves of SF' particles at 25°C using KNO_3 10^{-2} and 10^{-3} [mol dm^{-3}] as supporting electrolyte.

fraction dissolved, as does the titration method. Consequently, the dissolution or leaching of the SF' surface that occurs in the solid-liquid interface plays an important role in the surface properties of this material in aqueous media, even if this phenomenon takes place in atomic layers on the SF's surface.

The values of ζ -potential of SF as fibers using the streaming potential method showed very poor reproducibility. Nevertheless, the SF surface charge obtained by this method was negative for pH greater than 3, which agrees with the results found by electrophoresis.

In order to confirm that the difference between IEP and PZC is produced by the dissolution phenomena, the dissolution ratio of the element X (DR_X) was defined. In the computations the following expression was used :

$$DR_X = [X_{\text{Solution}}] [X_{\text{Slag Fiber}}]^{-1} \quad [3]$$

where X_{Solution} represents concentration [ppm] of the element X in the solution phase and $X_{\text{Slag Fiber}}$ indicates concentration [ppm] of the element X in SF before experimentation. Fig. 4 shows the DR_X as a function of initial pH at given conditions of temperature (25°C) and electrolyte concentration (10^{-3} [mol dm⁻³]) at 75 minutes. At low pH, all elements passed faster than Si_T to solution, which remains on the SF surface. This situation continues at a neutra range of pH due to Ca_T . Nevertheless, at high pH it is reverted. Consequently, the SF's surface became rich in amorphous SiO_2 in a wide range of pH (2 to 10). The IEP reported in the technical literature for amorphous silica is wide and highly dependent on the sample and procedure followed. Nevertheless, it has been reported

Fig. 4 Dissolution ratio (Eq. 3) as a function of initial pH, showing that the SF become rich in amorphous silica in a wide range of pH at 25°C in KNO_3 10^{-3} [mol dm⁻³] solutions at 75 minutes. Where (○), (□), (◇), (●) and (△) represent Ca_T , Mg_T , Al_T , Si_T and Fe_T , respectively.

to be approximately pH 2-3 under comparable conditions (36).

4. SUMMARY

The characteristics of the SF and its behavior in aqueous media were investigated on several instrumental techniques, experimental results and thermodynamic considerations. The main results may be summarized as follows :

- i) The distribution of main oxides presents in the SF's composition (SiO_2 , MgO and Al_2O_3) is constant and uniform in the SF, which generates sites with positive and negative charges depending of the compound located in the site.
- ii) The dissolution behavior (ppm order) of SF in a wide range of pH (4 to 10) and temperature (25 to 95°C) is negligible. The dissolution of SF' silica is understood by different leaching rates of atomic layers of the SF, which is highly dependent of the solutions' pH.
- iii) The differential dissolution of atomic layers onto the SF's surface produces a remarkably high difference between its PZC (pH 10.8) and its IEP (pH 2.9).

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