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Effects of surface Fe(III) oxides in a steel slag on the formation of humic-like dark-colored polymers by the polycondensation of humic precursors

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Abstract

Carbonated furnace steel slag is effective in enhancing polycondensation reactions of humic precursors such as quinones, amino acids and saccharides. To obtain more detailed information concerning the nature of the catalytic sites on the surface of slag, a pristine slag sample was treated with HNO₃, HF and NH₂OH to alter the surface states. The catalytic activities for the formation of humic-like dark-colored polymers were significantly decreased for the samples treated with HNO₃ or HF compared to untreated slag. Because substantial amounts of iron were eluted as the result of the HNO₃ and HF treatments, the minerals remaining on the surface of steel slag were characterized by XRD and SEM, and the results were compared with untreated slag. XRD patterns indicated the significant decrease in Fe(III) oxide content, including magnetite and hematite, as the result of the HNO₃ and HF treatment. In addition, when untreated slag

was reacted with humic precursors, the hematite and magnetite were largely eluted as a result of the reaction. These results support the conclusion that Fe(III)-oxides on the surface of steel slag, such as hematite and magnetite, serve as catalytic sites for enhancing catalytic activity for the formation of humic-like dark colored-polymers from humic precursors.

Keywords: Acid leaching; Catalytic activity; Fe(III) oxides; Humic precursors; Polycondensation; Steel slag

1. Introduction

It is generally accepted that humic substances (HSs) comprise one of the fractions of soil organic matter and serve as a pool of carbon in the geosphere. In HS formation, biomacromolecules such as proteins, polysaccharides, lignins and polyphenols are hydrolyzed to low-molecular-weight compounds such as amino acids, sugar and quinone, which are referred to as humic precursors. These precursors are subsequently recombined via polycondensation reactions to form humic-like dark-colored polymers [1-3]. It has been reported that minerals in soil can influence the formation of dark-colored polymers that are formed by the polycondensation of humic precursors. For example, birnessite, kaolin and nontronite have been reported to enhance the formation of dark-colored polymer from amino acids and quinones [4-9]. In addition, oxides of Si, Mn, Al and Fe have also been reported to facilitate the darkening of reaction mixtures that contain humic precursors [10, 11]. While allophanic soil, zeolites and bentonite are also able to enhance these reactions, their effects can be attributed to the fact that transition metals such as Ti and Fe that are present in the minerals, serve as Lewis acid catalysts, which also promote such polycondensation reactions [12-14].

Such minerals are applicable to the composting of raw organic wastes [15]. However, such minerals are expensive and the transition metal contents vary with the origin of the sample.

On the other hand, steel slag is a major by-product produced during the production of steel and is available at a relatively low cost [16]. Steel slag contains high levels of iron that can serve as a Lewis acid [17, 18]. Steel slag has been used in the production of coarse materials, coarse aggregates [19, 20] and as a fertilizer [21]. Steel slag contains CaO derived from lime and this may be harmful due to its basic nature. Thus, when utilizing slag as a fertilizer, it should be first neutralized with CO₂ (carbonated slag) [22]. We previously reported that carbonated steel slag was effective in terms of enhancing the polycondensation of humic precursors such as catechol, glycine and glucose to form humic-like dark-colored polymers [23, 24]. Although the majority of past studies reported on the effects of the catalytic powers of inorganic elements (Fe, Al, Mn and Si) in minerals [5, 9-11, 13, 14, 24], detailed information on the species of active elements that can enhance the polycondensation reactions is not available. In the present study, to investigate the active metal species that are present on the surface of steel slag, slag samples were treated with mineral acids (HNO₃ and HF) and a reducing agent (NH₂OH). The majority of metals on the surface of a slag sample (Al, Fe, Mn, and Ca) can be eluted by HNO₃. Si as well as Al, Fe, and Mn are further eluted by HF, while Ca is deposited in the form of CaF₂. NH₂OH is known to function as a reducing agent for eluting amorphous metal oxides such as manganese oxides from soils [25]. Thus, the majority of metal species that can serve as catalytic sites were eluted from the steel slag samples, and this would be expected to result in a decreased level of polycondensation reactions of humic precursors. In the present study, the catalytic activities for the

formation of humic-like dark-colored polymers from humic precursors were compared with the surface properties of the treated slag samples.

2. Materials and methods

2.1. Reagents and Materials

Catechol (>99% purity) was purchased from Tokyo Chemical Industry. Glycine (>99% purity) and glucose (>99% purity) were purchased from Nacalai Tesque. Ultra-pure water, prepared by a Millipore ultra-pure water system from distilled water, was used in all experiments. The steel slag was a carbonated basic oxygen furnace slag and was obtained from the Tetsugen Corporation (Muroran, Japan). Calcite and hematite were purchased from Wako Pure Chemical Industry, and magnetite was obtained at Tosashimizu (Japan). Prior to use, the steel slag and all coarse minerals were crushed with a mortar and pestle, followed by passing through a specific sieve size (62 μm). Particles with sizes under 62 μm were used in the tests. All other reagents (special reagent grade) were purchased from Nacalai Tesque and were used without further purification.

2.2. Treatment of steel slag with acids and reducing agent

To elute metals (Al, Ca, Mg, Mn and Fe), silicate and metal oxides (e.g., Fe_2O_3 and MnO_2), HNO_3 (1.0 M), HF (1.0 M) and NH_2OH (1.0 M) were employed as eluents, respectively. A 6 g sample of the untreated slag was placed to a 50 mL plastic centrifuge tube and the 30 mL aliquot of the eluent was then added. After shaking for 24 h at 160 rpm, the solid was separated by centrifugation (10,000 rpm for 10 min). After removing the liquid supernatant, a fresh 30 mL aliquot of eluent was added and the mixture again

subjected to a 24 h shaking. This procedure was repeated 6 times. The inorganic elements (Al, Ca, Si, Fe, Mn, and Mg) in the collected supernatants were analyzed using a Shimadzu ICPE-9000 type Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). The solid was washed with ultra-pure water 3 times, and then dialyzed against pure water using a cellulose dialysis tube (Sanko Junyaku Co., Ltd). The powdered slag sample was obtained after freeze-drying.

2.3. Analysis of slag

2.3.1 Inorganic elemental composition

The wet-digestion of slag samples (20 mg) was carried out using concentrated HCl (6 mL), HNO₃ (2 mL) and HF (2 mL) in a closed Teflon vessel, which was introduced into a microwave oven (Ethos Touch Control, Milestone General Co.,Ltd.). The temperature protocol was as follows: 0-220°C at a heating rate of 8.8 °C min⁻¹; 220 °C for 35 min. After the wet-digestion, to prevent the volatilization of SiF₄ and to protect the plasma quartz torch of the ICE-AES instrument, a 4% boric acid solution (15 mL) was added to the sample. The inorganic elements (Al, Ca, Mg, Mn, Fe and Si) in the solution were determined by ICP-AES.

2.3.2 XRD patterns

The X-ray powder diffraction patterns (XRD) of the samples were recorded by a Rigaku RINT 1200 type diffractometer using Cu K α radiation at a scanning speed of 0.05° min⁻¹. The slag samples were dried under reduced pressure (26.6 kPa) at room temperature before the measurements.

2.3.3 Specific surface area

The specific surface areas of the slag samples were determined by a N₂-BET method

using a Beckman Coulter SA3100-type instrument. The slag samples were dried under reduced pressure at room temperature before the measurements.

2.3.4. Scanning electron microscope

The powdered sample was placed on a carbon tape attached to an aluminum sample stage. The surface of the slag sample was then observed using a JEOL JSM-6510L type scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) under following conditions: working distance, 10 mm; accelerating voltage, 10 kV, magnification, $\times 1000$ or $\times 6500$.

2.4 Monitoring the polycondensation reaction of humic precursor

All glassware and ultra-pure water were autoclaved (120 °C for 20 min) prior to use. A 180 mL aliquot of autoclaved $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ buffer (0.2 M, pH 6.00 \pm 0.05) containing 0.02% (w/v) thimerosal as a sterilizer was placed in a 300 mL Erlenmeyer flask. The 2 g powdered slag sample or mineral (calcite, hematite or magnetite) was then added. Powdered catechol, glycine and glucose were added to the suspensions (final concentrations of 5 mM). The mixture was shaken at 160 rpm for 3 weeks, and the temperature was maintained at 25 °C using an FMS100-type incubator (EYELA). A 1 mL aliquot of the reaction mixture was removed at 0, 6, 24, 48, 72, 168, 336 and 504 h, and the mixture was then centrifuged at 10,000 rpm for 1 min. A 150- μL aliquot of the supernatant was diluted to 5 mL with ultra-pure water, and UV-vis absorption spectra (200 – 800 nm) were recorded using a V-630 type spectrophotometer (Japan Spectroscopic Co., Ltd.) with a quartz cell (1 \times 1cm) at 25°C. A 0.7 mL aliquot of the remaining supernatant was diluted to 20 mL with ultra-pure water, and the concentration of total organic carbon (TOC) was then measured using a Shimadzu TOC-V CSH-type

analyzer. In addition, after a 3-week incubation period, a 1 mL aliquot of the supernatant was diluted to 5 or 10 mL with aqueous 0.1 M HNO₃. After filtering through a 0.45- μ m membrane filter, the inorganic elements (Al, Si, Mg, Mn, Fe and Ti) were analyzed by ICP-AES. In addition, complex species of iron in the reaction mixtures were determined by the separation using a cation-exchange resin/ICP-AES method, as described in a previous report [26].

2.5. Separation and analyses of humic-like acids

After a 3-week incubation, the reaction mixture was centrifuged at 10,000 rpm for 15 min and the supernatant was filtered through filter paper (Advantec, No. 5C, Tokyo, Japan). The filtrate was then acidified to pH 1 with concentrated HCl. After standing for 1 day, the slurry was centrifuged at 10,000 rpm for 15 min. The precipitate, which contained humic-like acids (HLA), was re-dissolved in 0.1 M NaOH, and this was then treated with concentrated HCl (3 mL) and HF (3 mL) to remove traces of remaining minerals. After stirring for 1 day, the slurry was centrifuged at 10,000 rpm for 15 min, and the resulting precipitate, HLA, was dialyzed against pure water using a Spectra-Pore dialysis tube (nominal molecular weight cut-off of 500 Da). Powdered HLA was obtained by freeze-drying. The low-molecular-weight byproducts in the acidified supernatant were analyzed by the GC/MS after extraction with ethyl acetate, as described in a previous report [11].

The elemental compositions (C, H, N, and ash content) for the HLA samples were determined using a Micro Corder JM10 type elemental analyzer (J-Science Laboratory, Kyoto). The percentage of oxygen was calculated by subtracting the sum of C, H, and N from 100. The molecular weights for the HLA samples were measured by

high-performance size exclusion chromatography using a TSK-Gel α -M column, (7.8 mm i.d.×300 mm, void volume of 6.30 mL, Tosoh Co., Ltd.), following procedures described in a previous report [14].

Results and Discussion

3.1 Characterization of untreated and treated slag samples

The compositions of inorganic elements for the untreated and treated slag samples are summarized in Table 1. The untreated slag was mainly comprised of Ca, Fe, Si and a few percent of Al, Mn and Mg. As shown in the XRD patterns for the untreated slag (Fig. 1a), peaks corresponding to calcite (CaCO_3) were observed in the XRD pattern for the untreated slag, and peaks for various types of iron oxide, such as wustite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3), were also observed. Peaks corresponding to silicates were not found. It has been reported that minerals contained by slag, which had not been treated with CO_2 , are calcite (CaCO_3), $\text{Ca}(\text{OH})_2$, Ca_2SiO_4 , magnetite (Fe_3O_4), hematite (Fe_2O_3) and quartz [27]. Because the steel slag used in the present study was neutralized with CO_2 , Ca was mainly present in the form of calcite (CaCO_3), suggesting that silicates or silicon are present as non-crystalline forms.

Figure 2 shows the percentages of the inorganic elements removed by the treatments. The percents of the inorganic elements eluted from the steel slag were calculated as:

Elution (%) =

$$\{\text{Eluted metal (g L}^{-1})\} \times \{\text{Eluent volume (L)}\} / \{\text{Metal in the untreated slag (g)}\} \times 100 \quad (1)$$

Although elution of Fe and Mn oxides were expected in the NH_2OH treatment, no significant elution of Fe was observed and no alterations in the Fe-oxide peaks in XRD patterns were observed. However, 10 – 13 % of the Mn, Ca and Mg were eluted. In the

HNO₃ treatment, significant amounts of Ca (80%) and Fe (40%) were eluted. In the XRD pattern (Fig. 1c), the peaks corresponding to calcite and hematite had disappeared, but small amounts of wustite and magnetite remained. Large amounts of Fe and Si were eluted by the HF treatment. In the XRD patterns (Fig. 1d), the peaks for Fe-oxides disappeared, and most of the Ca was converted to fluorite (CaF₂).

The specific surface areas for the treated slag samples (NH₂OH 66.4±0.8 m² g⁻¹; HNO₃ 292±12 m² g⁻¹; HF 68.3±6.5 m² g⁻¹) were significantly higher than that of the untreated slag (11.1±0.8 m² g⁻¹). In particular, the HNO₃ treatment resulted in an increased specific surface area, because metals on the surface had been eluted and converted into micro-particles due to the destruction of the crystalline structures.

3.2 Catalytic activities for slag samples

To evaluate the catalytic activities of the various slag samples, the formation of the dark-colored humic-like polymers via polycondensation reactions of humic precursors (catechol, glycine and glucose) was monitored, based on the degree of darkening of the reaction solution (E_{600}). In general, the E_{600} increases with the extent of darkening of the reaction mixture in a polycondensation reaction [28]. The E_{600} value can be calculated from the light absorption coefficient at 600 nm, using the following equation [11, 13, 14]:

$$E_{600} (\text{L g}^{-1} \text{ cm}^{-1}) = \frac{\{\text{Absorbance at 600 nm}\}}{\{\text{Light path length (1 cm)}\} \times \{\text{TOC (g L}^{-1})\}} \quad (2)$$

Figure 3 shows the kinetic curves for the variations in E_{600} value. The E_{600} values in the presence of the untreated slag were much larger than those in its absence (control), indicating that the polycondensation reactions were enhanced to a considerable extent.

In the case of the NH_2OH treated slag, the reaction rate decreased slightly, compared to the untreated slag. This may be due to the loss of Mn, which can serve as a Lewis acid. The E_{600} value for the HNO_3 and HF treated slag samples were significantly smaller than those for the untreated slag, consistent with the elution of Ca, Fe, Si, Al and Mn.

Figure 4 shows UV-vis absorption spectra of reaction mixtures after a 3-week period of incubation. In general, UV-vis absorption spectra of soil humic acids show absorption bands for $n \rightarrow \pi^*$ electron transitions (200 – 210 nm) corresponding to carbonyl groups such as quinones and ketones and for a $\pi \rightarrow \pi^*$ electron transition (around 270 nm) corresponding to C=C double bonds in aromatic moieties [11]. The peak at 275 nm for the control sample was assigned to the $\pi \rightarrow \pi^*$ electron transition of catechol, and this peak was remained in the spectra of reaction mixtures for the HNO_3 and HF treated slag samples, indicating that polycondensation reactions of humic precursors were not extensive for these samples. However, in the presence of the untreated and NH_2OH -treated slag samples, the catechol peak disappeared and absorption bands at higher wavelength increased. An increased absorbance in the visible region (400 nm and 600 nm) for the catechol-glycine-glucose system was observed in the presence of birnessite ($\delta\text{-MnO}_2$) [8, 29, 30]. Thus, the results shown in Fig. 4 suggest that the catalytic powers for the untreated and NH_2OH treated slag samples are larger than those for the HNO_3 and HF treated samples.

In polycondensation reactions of humic precursors, the nitrogen in amino acids can add to nucleophilic carbons in aromatic rings and carbonyl carbons [11, 14]. Bosetto et al. [31] reported that C/N ratios and molecular weights of humification products produced via the Maillard reaction of glucose and glycine decreased and increased during the incubation, respectively. The order of the N/C molar ratio was determined to

be as follows; untreated > NH₂OH > HNO₃ > HF. In addition, the N-based yields for the HLA samples were calculated from the nitrogen contents using the following equation [14]:

$$\text{Yield of N (\%)} = \{\text{N in HLA (g)}\} / \{\text{Total N in the reaction mixture (g)}\} \quad (3)$$

The order of calculated N-based yield was as follows; untreated (9.44%) > NH₂OH (5.09%) > HNO₃ (2.89%) > HF (1.83%), consistent with the trend for the N/C ratio. These results indicate that the condensation of glycine with catechol and/or glucose was decreased in the HNO₃ and HF treated slag samples. In addition, the number average (M_n) and weight-average (M_w) molecular weights for polymers produced in the presence of the HNO₃ and HF treated slag were significantly lower than those for the untreated slag (Table 2). These results support the trend for the HNO₃ and HF treated slag samples, where large amounts of metals and metal oxides were lost, resulting in a decrease in catalytic activity for the polycondensation of humic precursors.

3.3. Mineral composition of slag samples after the reaction

For the HNO₃ treated slag, large amounts of Ca, Fe, Al, Mg and Mn were removed by elution, while a significant elution of Fe, Si, Mg and Mn was found in the case of the HF eluted sample. Thus, the large decreases in catalytic activities for the polycondensation reactions can be attributed to the loss of Ca, Fe, Si, Al, Mg and Mn. To elucidate the mineral compositions related to such elements, XRD patterns were observed after the reaction (Fig. 5). However, no significant alterations in the XRD patterns were observed after the reactions for the cases of the HNO₃ and HF treated slag samples (Fig. 5c and d), compared to those before the reaction (Fig. 1c and d). These results suggest that treatments with HNO₃ and HF result in a significant loss of

iron-oxides and this leads to a decrease in the reactivity of the polycondensation reactions. For the XRD patterns of the untreated and NH_2OH treated slag samples, the peaks for calcite, hematite and magnetite before the reaction (Fig.1a and 1b) were decreased substantially after the reaction (Fig. 5a and b). Thus, calcite, magnetite and hematite may contribute to the enhanced polycondensation reactions of humic precursors.

Figure 6 shows the progress of the reaction, based on E_{600} , in the presence of calcite, magnetite and hematite. For the case of calcite, the pH of the reaction mixture increased from 6 to 9 during the incubation. The control data indicated that the higher pH of 9 brought about a darkening of the reaction mixture via the auto-oxidation of catechol leading to a higher E_{600} . Thus, for calcite, the pH was adjusted to 6 by diluting the solution with an aqueous solution of H_3PO_4 at 6 h intervals. Although the E_{600} values for calcite were increased somewhat, compared to those for control, the E_{600} values for magnetite and hematite were much larger than those for the control and calcite. These results show that iron oxides, such as hematite and magnetite, on the surface of the steel slag can serve as catalytic sites for promoting the formation of humic-like dark-colored polymers via polycondensation reactions of humic precursors.

3.4. Surface alterations of the slag sample before and after the reaction

Figure 7 shows the SEM images of the untreated slag. Before the reaction, fine particles were adsorbed to the surface of the larger particles. However, small fine particles disappeared and glossy filamentous lumps appeared after the reaction. Figure 7 also shows the elemental mapping by EDS for the untreated slag before and after the reaction. In the SEM images and EDS mapping before the reaction (Fig. 7a-c), Ca and

Fe were separated. The SEM image and EDS mapping was focused on the glossy filamentous lump after the reaction (Fig. 7d). The EDS mapping of this part indicated that the glossy filamentous lump corresponded to Ca, related to brushite (CaHPO_4). As shown in elemental compositions determined by EDS analysis (Table 3), the surface content of Ca after the reaction was not smaller than that before the reaction. These results support the conclusion that Ca in calcite on the surface of the slag is transformed into brushite as a result of the reaction with phosphate buffer in the reaction mixture. Thus, when calcite is present in the slag, it cannot serve as a catalytic site for enhancing the polycondensation reactions.

On the other hand, the carbon content on the surface of the slag was increased after the reaction (Table 3). Humic substances can become adsorbed to iron oxides [32-34]. Thus, the formed HLA could become adsorbed to the surface of the slag as a result of polycondensation reactions. Such interactions could result in the catalytic sites being covered, thus decreasing their catalytic power. Although the increase in E_{600} with the extent of polycondensation reactions reached a plateau (Fig. 3a and b), this can be attributed to the catalytic sites being covered, as the result of the adsorption of the formed HLA to the surface of humic-like substances.

3.5. Elution behaviors of iron from slag surfaces

The EDS mapping of Fe showed that the Fe content was decreased significantly after the reaction, compared to that beforehand. These results are consistent with the increase in eluted iron after the reaction (Table 4) and the surface iron contents, as analyzed by EDS (Table 3). It is possible to separate and isolate Fe(II) ions from iron(III)-oxides via complexation with quinone derivatives that are present in humic substances [26, 35, 36].

Thus, the complex species of iron in the catechol-glycine-glucose reaction mixtures were determined in the presence of untreated slag, and 94% of the total iron in the reaction mixture was present in the form of complex species. This suggests that the formed HLA or the initial materials (*i.e.*, catechol, glycine or glucose) can contribute to the elution of iron from the slag surface. To elucidate the influence of the initial materials on the elution of iron from the steel slag, catechol, glycine or glucose was reacted with the untreated slag for 4 days, a period that corresponds to the initial stage of the polycondensation reactions. Although no iron elution was observed in the presence of glycine and glucose alone, 0.73 mg L^{-1} of iron was eluted in the presence of catechol alone and 82% of the total iron was present as complex species. These results show that catechol plays an important role in the formation of iron-organic complexes as the origin of dark-colored materials. Based on these results, the reaction pathway for the formation of HLM are proposed, as shown in Fig. 8. Fe(III) ions are initially eluted from iron(III)-oxides, such as hematite and magnetite, via complexation with catechol. Catechol can easily reduce Fe(III) to Fe(II), which is then converted to oxidized species, quinone and semiquinone radicals. It has been reported that quinones and semiquinone radicals can promote the nucleophilic addition of the nitrogen atom in glycine to form humic-like substances [37, 38]. The nitrogen-carbon adducts (*a* and *b* in Fig. 8) were identified in the reaction mixture by GC/MS analysis after extraction with ethyl acetate. Such low-molecular-weight byproducts can be regarded as reaction intermediates and further be polymerized to form HLA. Thus, Fe(III)-oxides such as hematite and magnetite in the steel slag have the ability to serve as important catalytic sites that function to facilitate the polycondensation of humic precursors.

4. Conclusions

The influence of surface metal state on the polycondensation of humic precursor was investigated. Ca and Fe were largely eluted by treatment with HNO₃ and Fe and Si were largely eluted by an HF treatment. The treated slag samples failed to enhance the polycondensation reactions. In addition, XRD and SEM-EDS analyses indicated that the calcite, magnetite and hematite composition decreased as a result of polycondensation reactions. Magnetite and hematite enhanced the formation of dark-colored polymers. Thus, iron (III)-oxides (such as magnetite and hematite) on the surface of steel slag can serve as catalytic sites for enhancing the formation of humic-like dark-colored polymers that are produced via the polycondensation of humic precursors.

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Figure Captions

Fig. 1. XRD patterns for untreated (a), NH_2OH (b), HNO_3 (c) and HF (d) treated slag samples. Values represent the d-spacing for each mineral.

Fig. 2. Percents of the eluted inorganic elements from slag samples.

Fig. 3. Kinetics of E_{600} variations in the absence and presence of untreated and treated slag samples: (a) untreated (b) NH_2OH (c) HNO_3 (d) HF (e) without slag (control).

Fig. 4. UV-vis absorption spectra of reaction mixtures after a 3-week incubation period.

Fig. 5. XRD patterns for slag samples after the reaction: (a) untreated (b) NH_2OH (c) HNO_3 (d) HF. Values represent the d-spacing for each mineral.

Fig. 6. Kinetics of E_{600} variations in the presence of hematite (a), magnetite (b) calcite (c) and control(d)

Fig. 7. The results of elemental mapping for untreated slag by SEM-EDS before (a – c) and after (d – f) the reaction: (a) and (d) SEM images ($\times 6500$); (b) and (e), Ca mapping; (c) and (f), Fe mapping.

Fig. 8. Proposed pathways for the formation of HLA. The mass spectra assignments for byproducts, *a* and *b*, were as follows (m/z [fragments, relative intensity]): *a*, 252 [M, 11.6], 193 [M- CH_2COOH , 71.2], 151 [(M+1)-(CH₂COOH)(CH₃CO), 100]; *b*, 238 [M, 12.8], 179 [M- CH_2COOH , 100], 137 [(M+1)-(CH₂COOH)(CH₃CO), 86.5].

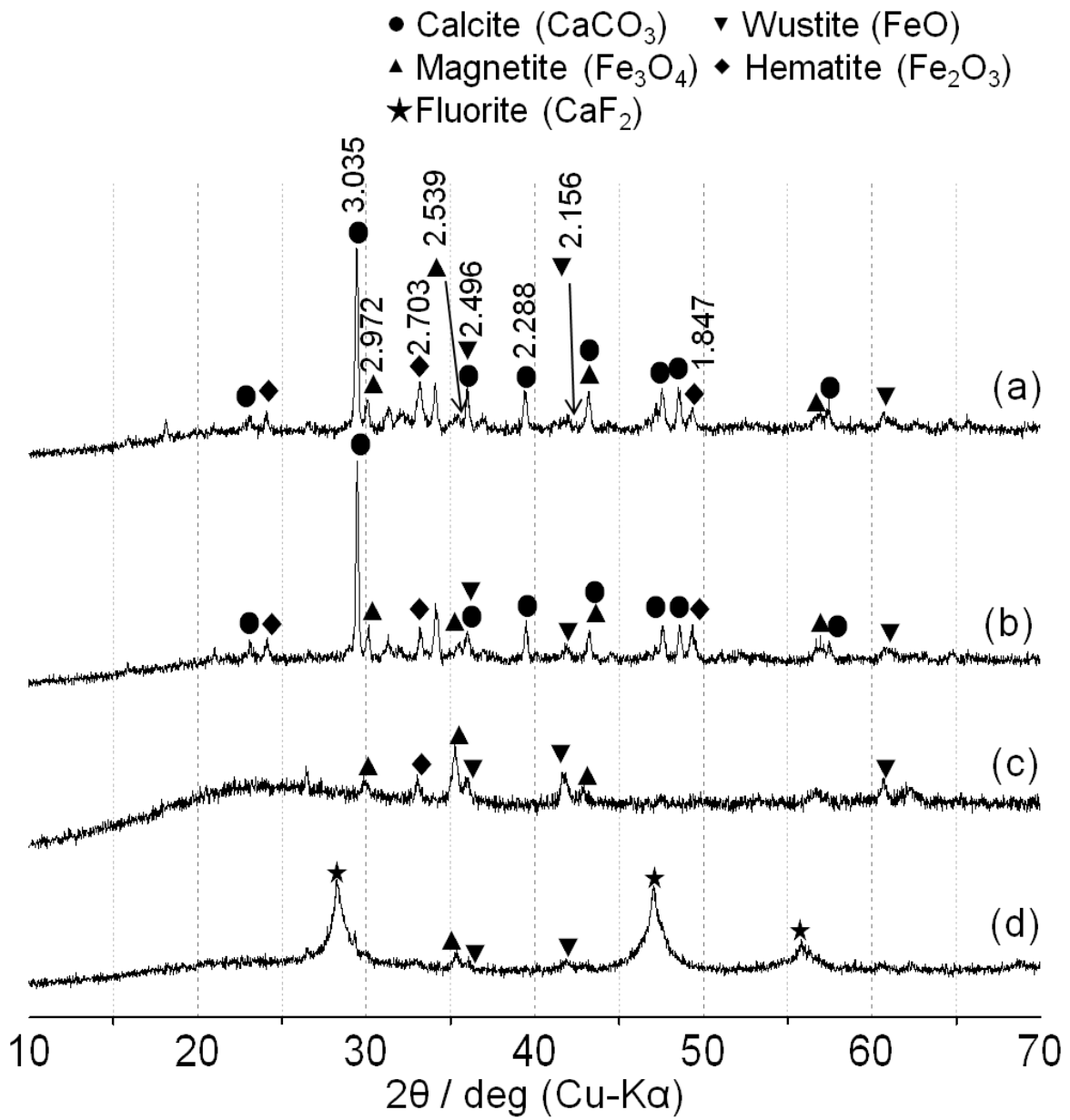


Fig. 1. COLSUA-D-12-00967R1

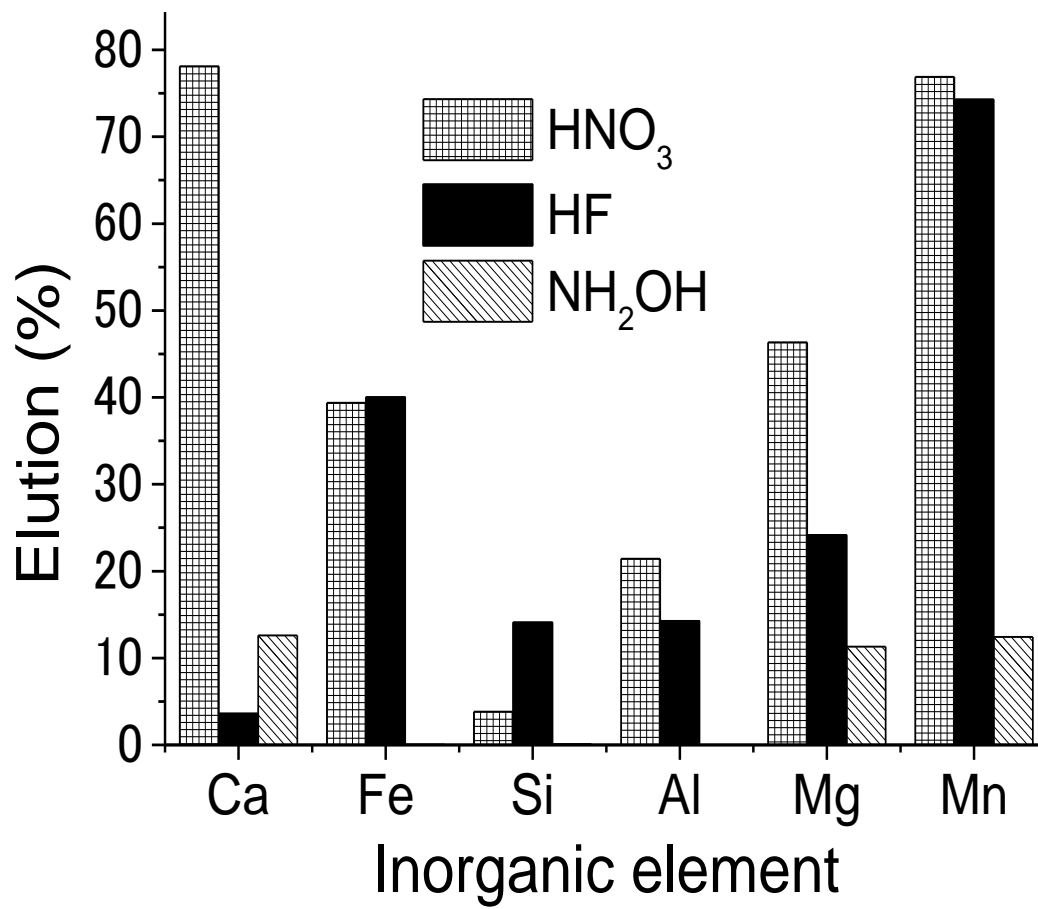


Fig. 2. COLSUA-D-12-00967R1

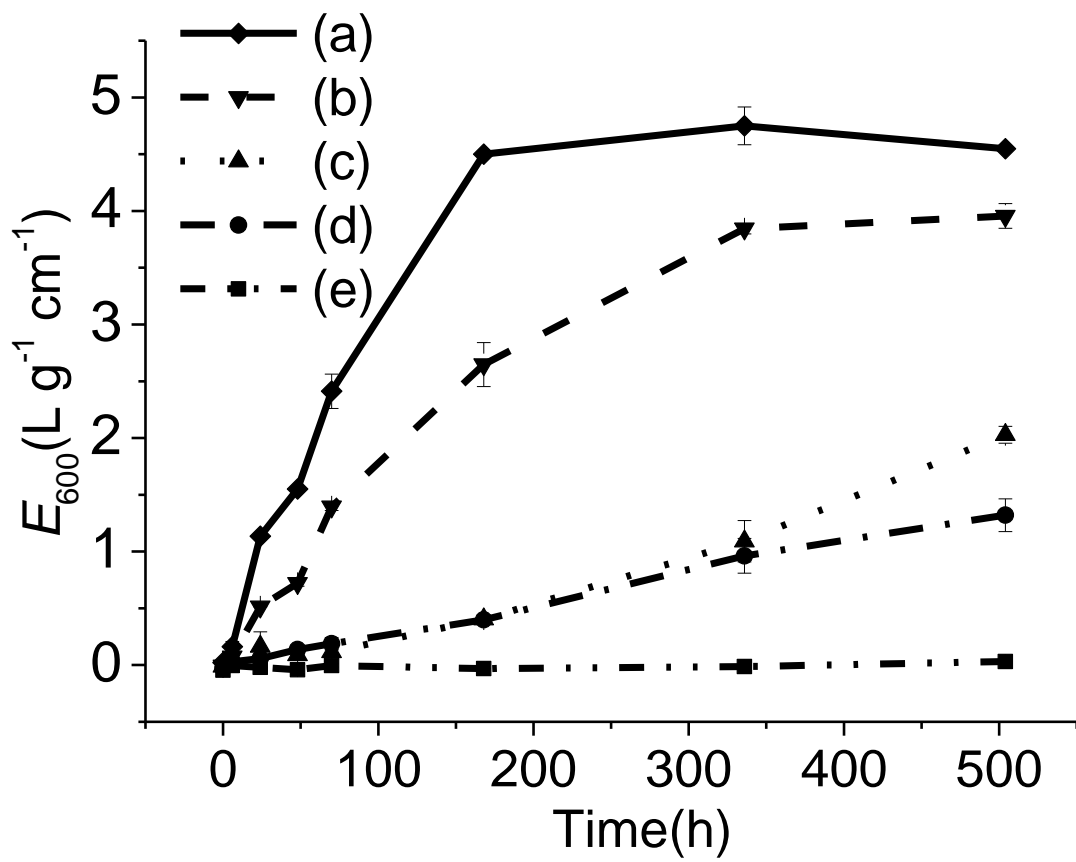


Fig. 3. COLSUA-D-12-00967R1

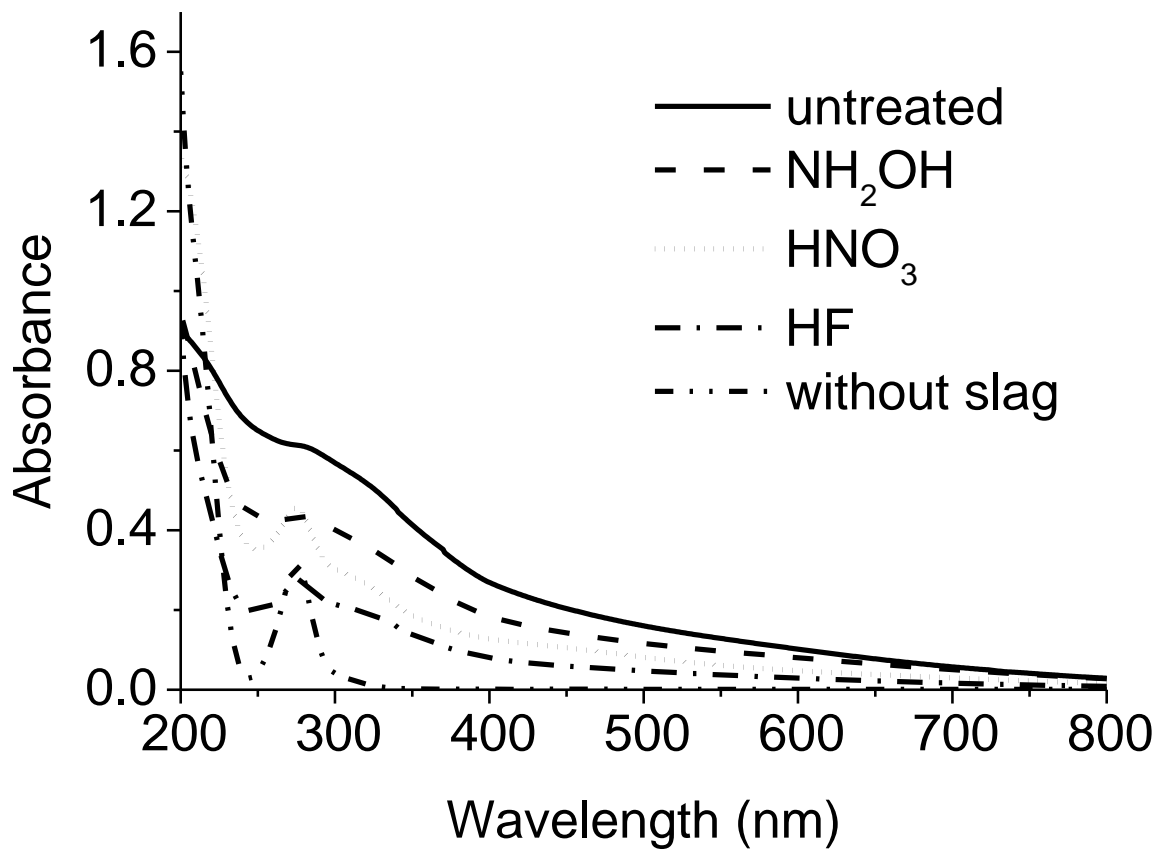


Fig. 4. COLSUA-D-12-00967R1

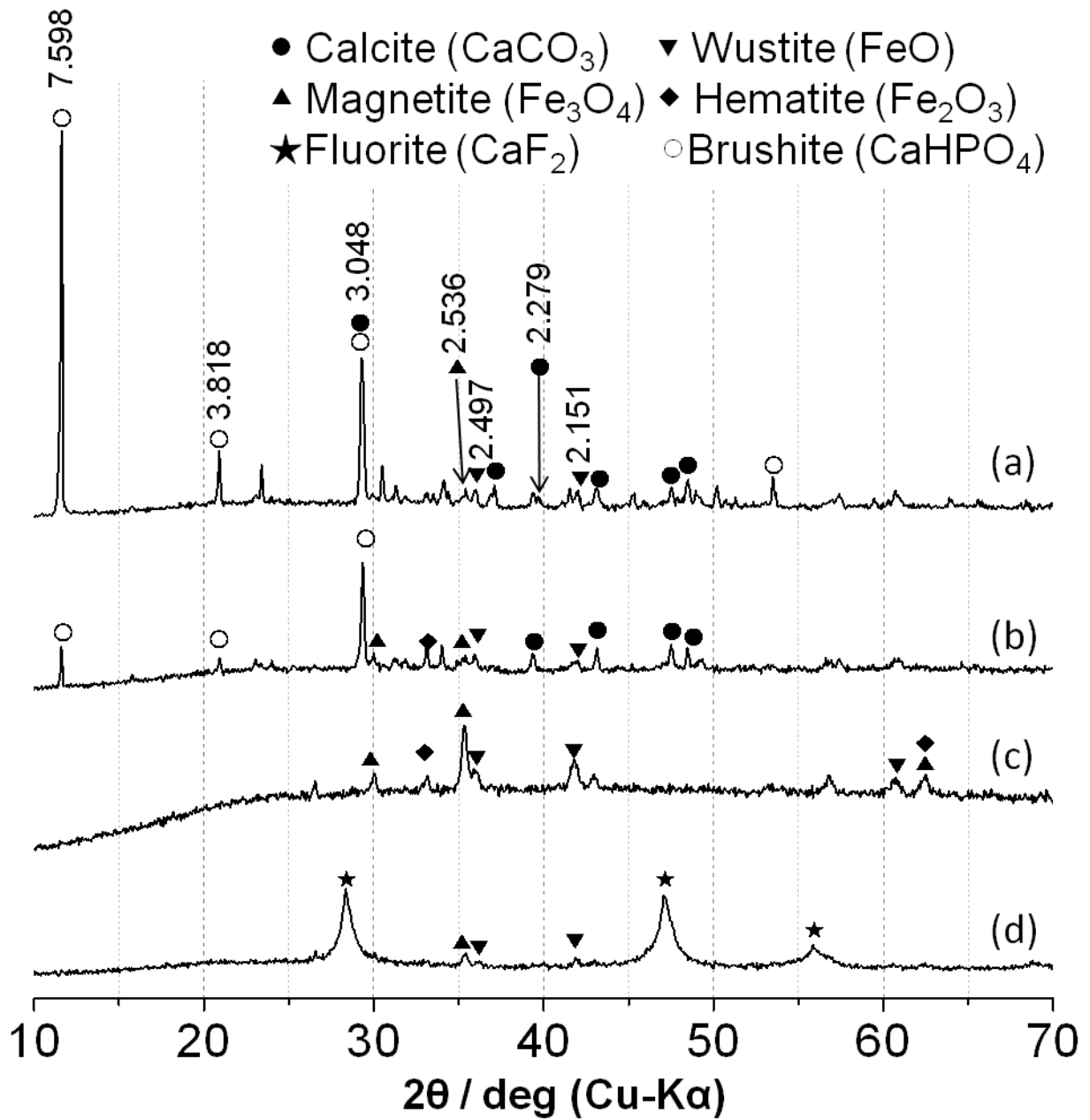


Fig. 5. COLSUA-D-12-00967R1

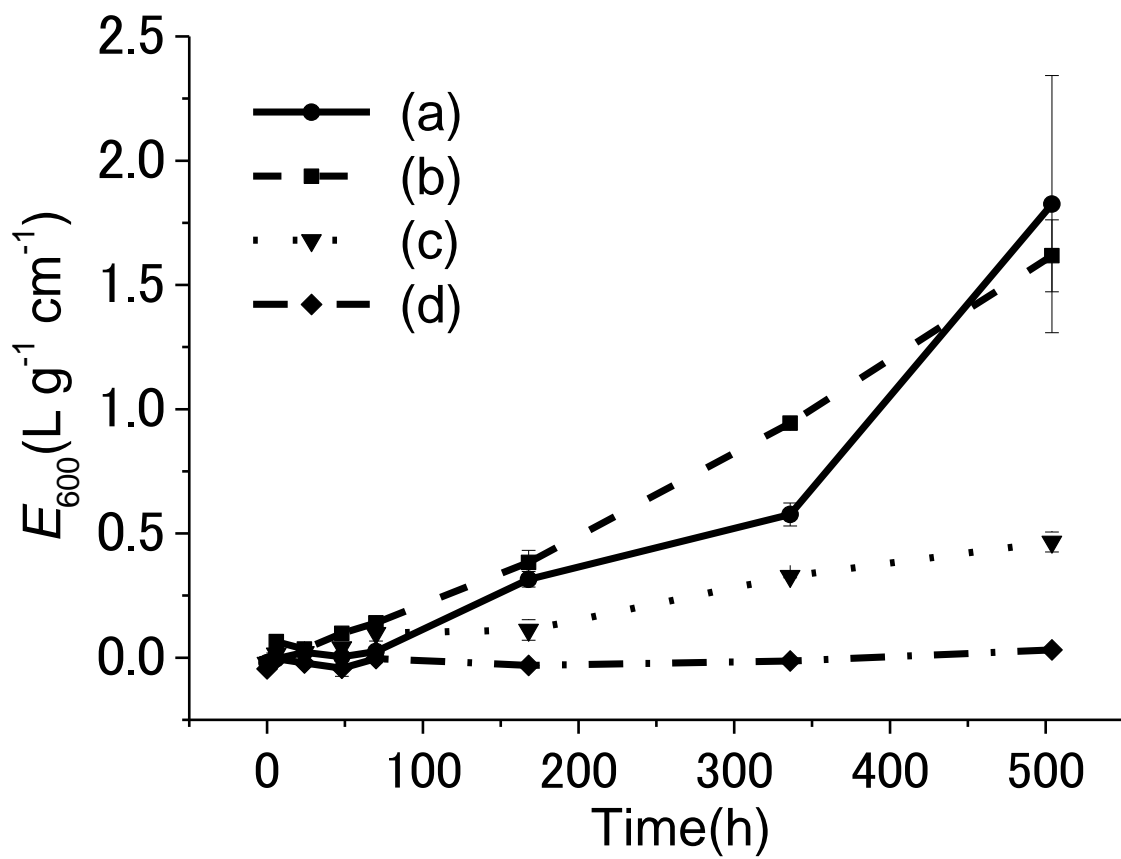


Fig. 6. COLSUA-D-12-00967R1

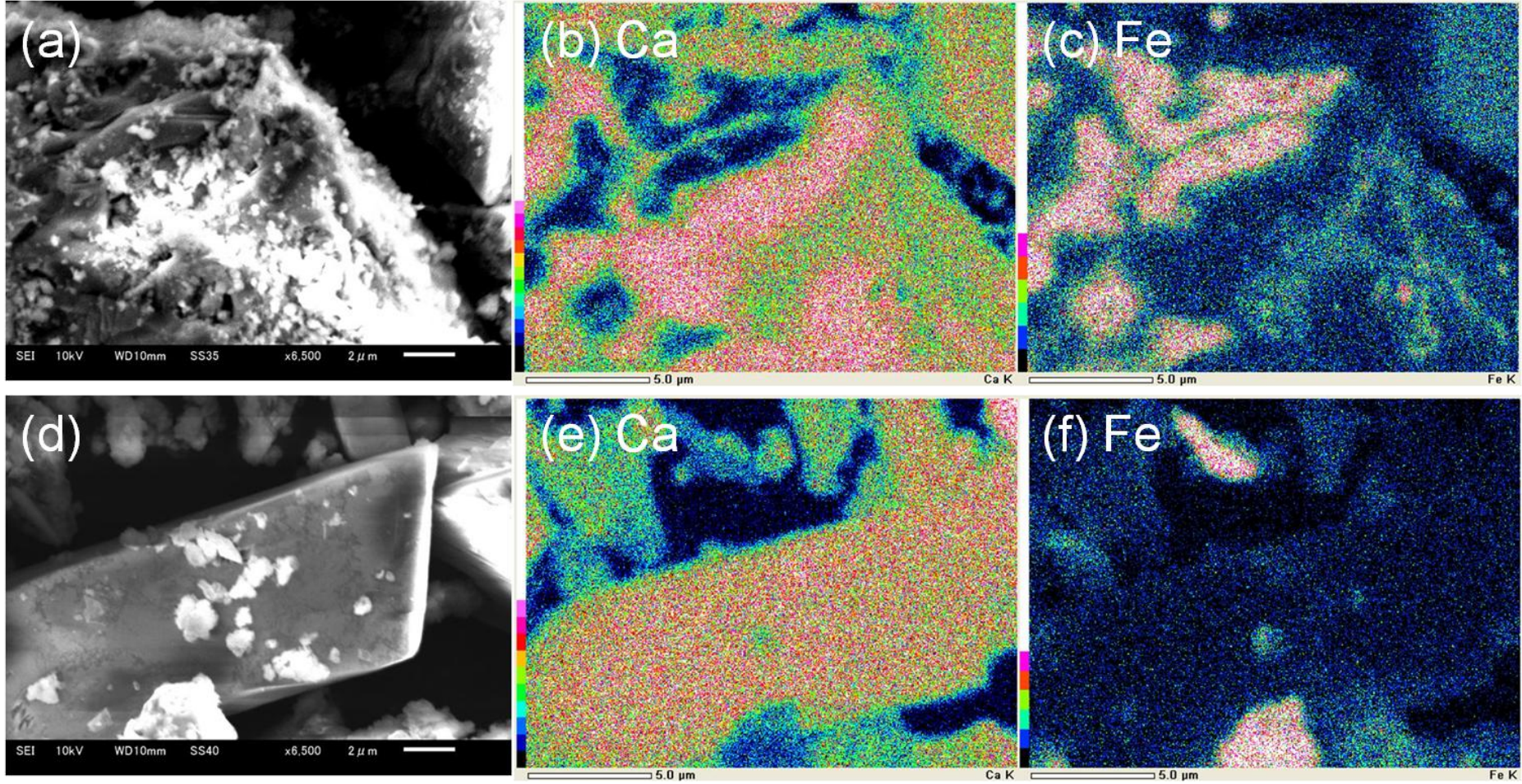


Fig. 7. COLSUA-D-12-00967R1

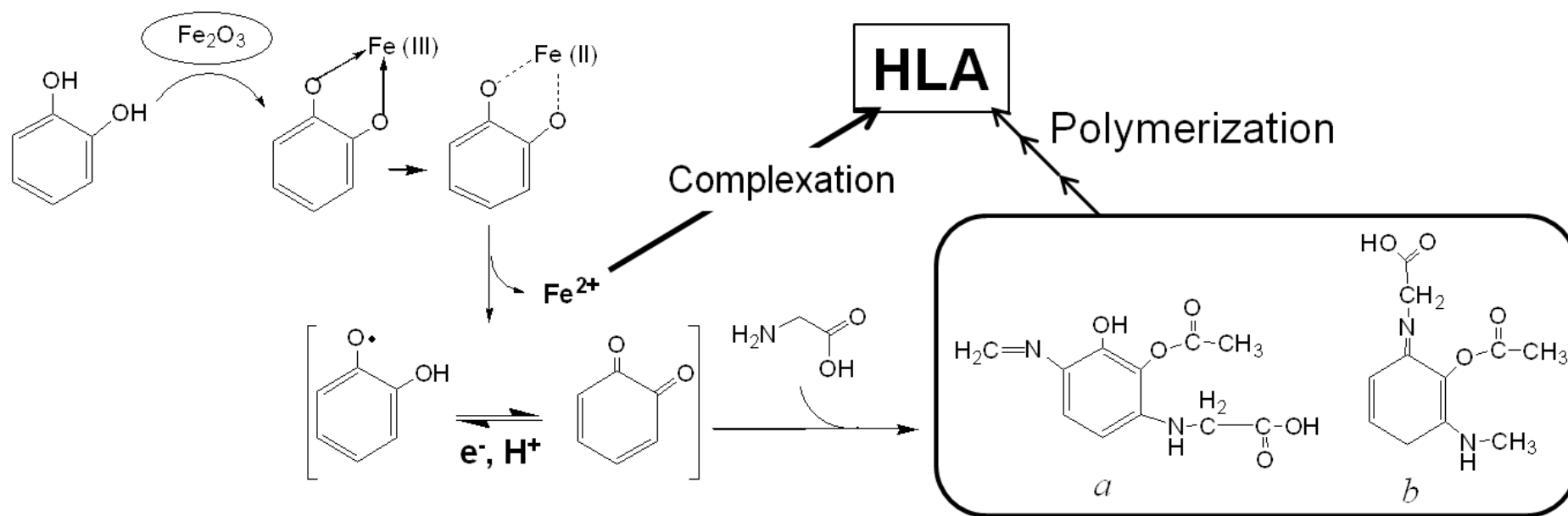


Fig. 8. COLSUA-D-12-00967R1

Table 1. Composition of inorganic elements for the untreated and treated slag samples (mg L^{-1}).

Slag Sample	Al	Ca	Fe	Mg	Mn	Si
Untreated	60.6±0.8	320±2	125±1	30.2±0.9	27.2±0.1	356±6
NH ₂ OH	58.9±1.1	231±3	152±3	19.7±0.3	27.3±0.5	460±7
HNO ₃	67.9±0.5	56.7±0.3	216±2	14.2±0.1	16.0±0.1	600±12
HF	71.0±1.1	290±5	84.6±1.5	15.2±0.2	6.06±0.12	389±5

Table 2. Elemental composition and molecular weights of the HLA samples.

Sample	Elemental composition (%)						Molecular weight	
	C	H	N	O	Ash	N/C	M_n	M_w
HLA-Untreated	46.88	2.91	1.68	44.53	4.00	0.0307	2081±280	3169±480
HLA-NH ₂ OH	42.07	2.71	1.34	44.08	9.80	0.0273	2074±80	3130±130
HLA-HNO ₃	41.42	2.60	0.87	45.51	9.60	0.0180	1535±70	2134±130
HLA-HF	45.17	2.82	1.00	44.40	6.61	0.0190	1729±90	2426±140

Table 3. Content of inorganic elements, as determined by EDS on the surface of the untreated slag before and after the reaction.

Sample	%C	%O	%P	%Al	%Ca	%Fe	%Mg	%Mn	%Si
Before	8.76	30.6	0.41	0.78	21.4	30.1	0.50	2.35	4.25
After	16.0	47.2	10.6	0.60	19.9	3.22	0.18	1.13	1.17

Table 4. Concentration of inorganic elements eluted from slag samples after a 3 week polycondensation reaction.

Sample	Concentration (mg L ⁻¹)					
	Al	Ca	Fe	Mg	Mn	Si
Untreated	37.49±4.81	72.1±1.60	3.17±0.06	66.8±0.6	12.0±0.1	110±0.4
NH ₂ OH	46.0±2.73	84.8±0.5	4.89±0.07	34.2±0.1	13.6±0.1	104±0
HNO ₃	n.d. ^a	3.00±0.28	6.86±0.26	1.23±0.05	1.37±0.04	43.8±0.3
HF	n.d. ^a	51.2±8.5	2.18±0.55	3.67±0.46	3.70±0.68	70.2±11.5

^aNot detected.