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EXTRACTION OF ACTIVE SILICON FROM THE IRON SLAG OF KAKCHING, MANIPUR TO UTILISE AS FERTILISER

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ABSTRACT

Iron slag is by-product generated during smelting process of iron. Slag is not considered as hazardous material but from an environmental point of view it is defined as waste. Slag contains silica as major component and silicon is an essential micronutrient with several advantages in the growth of farm plants such as rice, sugar cane, cassava and corn. To fully utilize such silicon nutrient, the slag has to be processed to acquire a soluble form of silica, the so-called "ortho-silicic acid". In the present work, innovative process for transforming slag to extract soluble silica in an active form has been developed. Soluble form of silica was prepared through an acid hydrolysis of slag concerned with acid conditions such as sulfuric acid system and a mixture system of perchloric acid and hydrochloric acid. Characterization of soluble silica compared with a commercial ortho-silicic acid was performed by FTIR spectra analysis. Extractability of soluble silica was investigated by using inductively coupled plasma-optical emission spectrometry (ICPOES) and X-ray fluorescence spectrometry (XRF) techniques.

The results showed that soluble silica in the form of ortho-silicic acid was productive when slag was processed with using sulfuric acid (H_2SO_4)*. By using a mixture of perchloric acid and hydrochloric acid, soluble silica was in the form of poly-silicic acid system. The obtained ATR FT-IR spectra of soluble silica were consistent with that of the commercial ortho-silicic acid. Absorption band of Si-O and Si-O-H, a prominent characteristic of ortho-silicic acid, were revealed at 1064* cm^{-1} *and 984* cm^{-1}*, respectively. Therefore, slag appears to be a promising source of using as fertilizer. 5.6% silicon could be extracted from iron slag in which a primary* *content of silicon is 14%. This, however, needs furthers optimizing acid hydrolysis conditions to achieve a superior extractability of soluble silica.*

Keywords: Iron slag, Slag Fertiliser, Silicic Acid, Ortho-Silicic Acid, Active Silicon, Soluble Silica, Agricultural Slag, Micro Nutrient Slag

1. INTRODUCTION

Slag, a by-product generated during manufacturing of pig iron and steel, is defined as “waste”. Therefore, its amount and disposal motivate an environmental concern. Nowadays, reduction or recycle of industrial waste as well as slag has been an intensive interest. Although utilization of slag in construction and civil engineer is a common practice, report of slag application in agricultural subject is still little. Because slag contains many useful elements for crops, such as silicon, magnesium, and aluminium, it is a potential source of plant nutrients. Especially, silicon is essential for rice, sugar cane, cassava, and corn. Since slag contains a high level of silicon, utilization of slag in crops is worth not only in the growth of plants but also improvement of their resistance to pests and diseases. Many studies of using slag in paddy, which made the rice production increases, have been reported. Silicon presents elsewhere in sand, soil, ore with a large amount, but in an inactive form of silica. Basically, silicon is absorbed by plants in an active form, whereas plants absorb silicon from the soil solution, which is usually very small. It takes very long time up to a year in naturally transforming silica to be absorbed by plants.

In this study, an extractability of active silicon form slag, focusing iron slag and steel slag, has been studied by acid hydrolysis of slag using acid. Validation of active silicon was perform by means of attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR), inductive coupled plasma-optical emission spectrometry (ICP-OES), and X-ray fluorescence spectrometry (XRF) method.

2. BACKGROUND

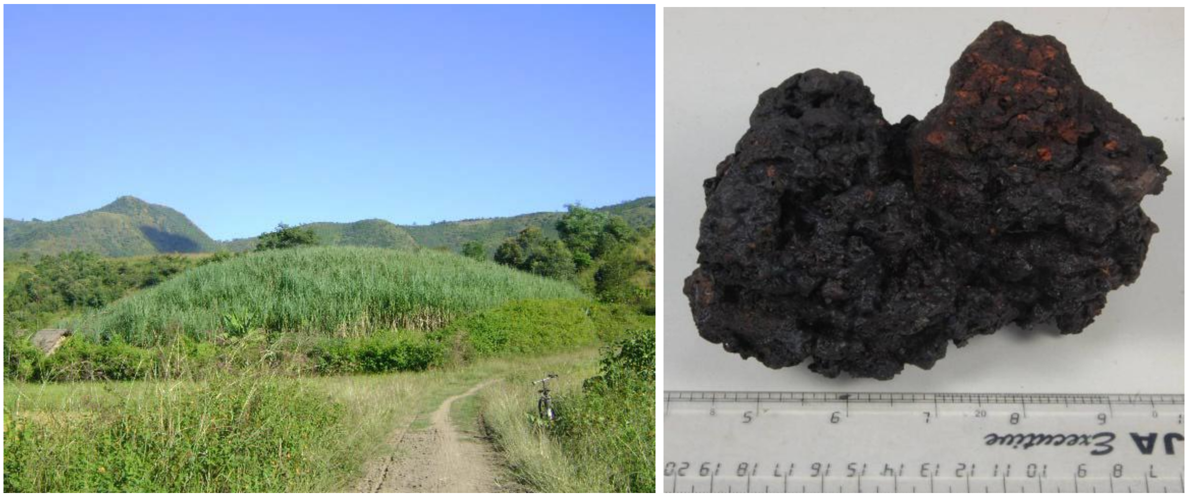

Figure – 1: standing sugarcane crop grown effectively at Tumu Ching, Kakching, Manipur, India and piece of lumpy iron slag excavated from the soil where sugar canes are grown throughout the year.

The site locally known as Tumu Ching lies in an area which according to historical records is famous for ancient iron smelting. It lies about 70Km east of Imphal the capital city of Manipur and is just about 40 Km away from the Indo – Myanmar border. The site was discovered in November 2008 by our team. The area is full of slag. Historical records tell us that when King Khuiyok Tompok (154 A.D.-264 A.D.) was having a tour to Kakching, iron deposits were found at this place. This reveals that iron deposits were found prior to this period. During excavation just below the surface two large pieces of slag that formed the ancient furnace could be found.

The smelting site is located just at the foothill of the series of ranges connecting those mountains in the Chandel District which extends up to Myanmar in the South eastern side. The small hill-ock which is full of slag might have been formed by deposition of slag produced out of the long run smelting process. The huge amount of slag obtained in the area reveals that there might be a big furnace just below the surface.

The proposed research work will really help in establishment of some facts on the ancient iron industry in Manipur, the techniques used in the smelting, the methodology and any rituals followed in the entire process of smelting. Further investigation will help in locating the ore sites, may be in the adjoining hills from where the ancient smelters used to collect ores, brought there and did the smelting to extract iron in traditional methods.

Primarily, the slags consist of silicates and silicates of calcium, aluminium, magnesium, as well as other bases in various combinations. Both iron slag and steel slag have unique physical and chemical properties that make them variety in applications. Their mineral contents, i.e., SiO_2, CaO, MgO, Mn and other micro nutrient, influence on the growth of plants. The active form, which can be absorbed by plants, of silicon is known as "ortho-silicic acid". Ortho-silicic acid contains only one silicon atom and formulated as H_4SiO_4.

3. EXPERIMENTAL METHODS

In the present study, an innovative process for extracting active silicon from iron slag and steel slag has been developed. The process was carried out by acid hydrolysis of slags. Characterization of active silicon was performed by ATR FT-IR spectra analysis. Composition and solubility of active silicon was determined by using ICP-OES and XRF techniques.

3.1. Composition of Iron Slag and Steel Slag

Iron slag and steel slag were pulverized in a mortar until achieve a particle size of 1-3 mm. The slags were further crushed by using Rocklabs IA-BT to get a homogeneous and smaller size. Weight iron slag and steel slag 7 g and mixed each with binder (cellulose) 3 g. Then, pressed each slag into an aluminum cup with diameter 37 mm by using HERZOG TP-40. The chemical compositions of slags were analyzed by using X-ray fluorescence spectrometer-PANalytical AXIOS installed with OMNIAN program.

3.2. Extraction of Active Silicon

A certain amount of iron slag and steel slag were each added by sulfuric acid and a mixture of perchloric acid and hydrochloric acid. Then, filtered the solutions by using filter paper no. 5A. The filtrate was diluted into 100 mL in volumetric flask.

3.3. Characterization of Active Silicon

ATR FT-IR spectra of iron slag, steel slag, samples prepared according to 3.2, and commercial ortho-silicic acid were obtained by a Nitolet 6700 spectrometer with DTGS detector. A slide-on Ge micro-IRE was installed into the spectrometer. Microscope-Reflectance mode was selected. The spectra were recorded from 4000 to 650 cm^{-1} with a spectral resolution of 4 cm^{-1}. 64 scans were co-added for a spectrum. Spectrum of Ge micro-IRE without sample was used as the background.

3.4. **Quantitative Analysis of Active Silicon**

3.4.1 Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Silicon standard solutions for calibration curve were prepared from 1000 mg/L PerkinElmer Pure standard solution. The solutions of 0, 1, 2.5 and 5 mL were pipetted into each volumetric flask and diluted to 50 mL. Pipetted the solutions in 3.2 500 µL and diluted to 10 mL in separated volumetric flasks. Weight commercial ortho-silicic acid 2 g and dissolved in distilled water 500 mL, stirred the solution. The solution was then filtered by filter paper no. 5A. The filtrate was diluted to 500 mL. Further pipette the solution of commercial ortho-silicic acid 500 µL and diluted to 10 mL. The crushed iron slag and steel slag were weighted 2 g and dissolved each in distilled water 20 mL, continuously stirred. Additional distilled water 50 mL was further added and mixed properly, and the solution was filtered afterwards. The filtrate was added by nitric acid 1.5 mL and diluted the solution to 100 mL. Further pipette the solution of each slag 500 µL and diluted to 10 mL in volumetric flask. Solutions of calibration standard solution, active silicon from iron slag and steel slag, commercial ortho-silicic acid, and original iron slag and steel slag were quantitative determined by using a sequentially scanning ICP-OES spectrometer, PerkinElmer-Optima 7000DV.

3.4.2 X-Ray Fluorescence Spectrometry (XRF)

Weight 7 g of dry powder of active silicon extracted from iron slag and commercial ortho-silicic acid, each mixed with binders 3 g. The samples were pressed into aluminum cup with diameter 37 mm and introduced into the XRF spectrometer in order to determine the compositions.

4. RESULTS AND DISCUSSION

4.1. Composition of Iron Slag and Steel Slag

The iron slag and steel slag used in this work were sampling from steel mills in Chonburi, Thailand. Steel slag was from EAF process. Composition of the slags is reported in Table I. Major components of slag are CaO, SiO_2 and Fe_2O_3, whereas considered amounts of silicon to be useful as plant nutrients. The iron content is the major difference between iron slag and steel slag. In iron slag, Fe_2O_3 is about 50%, whereas, in case of steel slag, it is 26%.

Table I: Compositions of iron slag and steel slag (%wt.).

Composition	iron slag	steel slag
Na_2O	0.04	0.19
MgO	4.4	5.3
Al_2O_3	3.7	7.7
SiO_2	10	24
P_2O_5	0.57	0.22
K_2O	0.01	0.45
CaO	22	29
TiO_2	0.55	0.76
Cr_2O_3	1.1	1.9
MnO	4.8	3.7
Fe_2O_3	50	26

4.2. Characterization of Active Silicon

It is well known that silicon in slag is in an inactive form of silica (SiO_2), which is insoluble. The active soluble silicon was extracted via acid hydrolysis of iron slag and steel slag. They are characterized in comparison to the slags without treatment as well as the commercial ortho-silicic acid. Infrared spectra of active silicon and original slags are predominant in two frequency ranges at 3700-3000 and 1700-850 cm^{-1} (Figure 1). A broad band between 3700-3000 cm^{-1} together with a sharp band at around 1640 cm^{-1} represents to a vibration of O-H from H_2O in stretching and bending mode, respectively. Difference in spectral feature is found in low frequency range at 1550-1350 and 1280-800 cm^{-1}, these correspond to an absorption band of C-O and Si-O, respectively (Figure 2). A vibrational band of C-O stretching mode from CO_3^{2-} at around 1450 cm^{-1} are presented in the spectra of iron slag and steel slag before treated with acid. This band disappears after performing acid hydrolysis. A strong sharp band of Si-O from silica (SiO_2) at 1130 cm^{-1} is observed in spectrum of iron slag, whereas this band appears as a small shoulder in overlapping with a strong band of Ca-O at 1000 cm^{-1} in spectrum of steel slag. After performing acid hydrolysis of iron slag with H_4ClO_4 + HCl and H_2SO_4, the peak of Si-O is shifted to lower frequency at 1090 and 1064 cm^{-1}, respectively. The latter is more consistent to spectrum of commercial ortho-silcic acid. Shifts of Si-O peak due to chemical changes of silicon component from inactive form to the active one. A band at 984 cm^{-1} corresponds to Si-O-H stretching vibration and indicates the present in commercial product is also observed in spectrum of iron slag after treated with H_2SO_4, but this band is not found after treated with a mixture acid. This might be due to extracted active silicon by using mixture acid is in polymeric form. Likewise, after performing acid hydrolysis of steel slag with H_2SO_4, the absorption band of Si-O is also shifted to higher frequency at 1060 cm^{-1}, which is consistent to that of commercial product. Additionally, a band at around 910 cm^{-1}, is observed as a strong sharp band in spectrum of treated steel slag and found to be a small broad band in treated iron slag spectrum. This band could be assigned to a vibrational band of Si-O-Al and Si-O-Mg segment. Therefore, acid hydrolysis of slags using H_2SO_4 found to be promising to extract active silicon from iron slag and steel slag, whereas the active silicic acid system containing Al and Mg.

4.3 Solubility of Active Silicon

Solubility of active silicon extracted from iron slag and steel are determined in comparison to that of slag before treatment and commercial product by using ICP-OES method, the result is shown in Table II. Without treated with acid, silicon in iron slag and steel slag can hardly dissolve in H_2O. In contradictory, silicon of commercial ortho-silicic acid can be dissolved easily in H_2O, in which 5.4% could be soluble from the product with silicon 7.4%. 5.6% silicon could be extracted from iron slag in which a primary content of silicon is 14% (40% extraction). In steel slag, 3% silicon was extracted according to 11% of silicon content (27% extraction). This, however, needs furthers optimizing the hydrolysis conditions to achieve a superior extractability of soluble silica. Composition of active silicon has also been determined in comparison to that of the commercial product, as shown in Table III. Besides silicon other elements, such as 4.4% aluminium (Al) and 2.8% magnesium (Mg), as well as small amount of sodium (Na), potassium (K), calcium (Ca), manganese (Mn) and iron (Fe) could be obtained as well. These elements are known as micro-nutrient for corps and also found in commercial product of active silicon even differ in content.

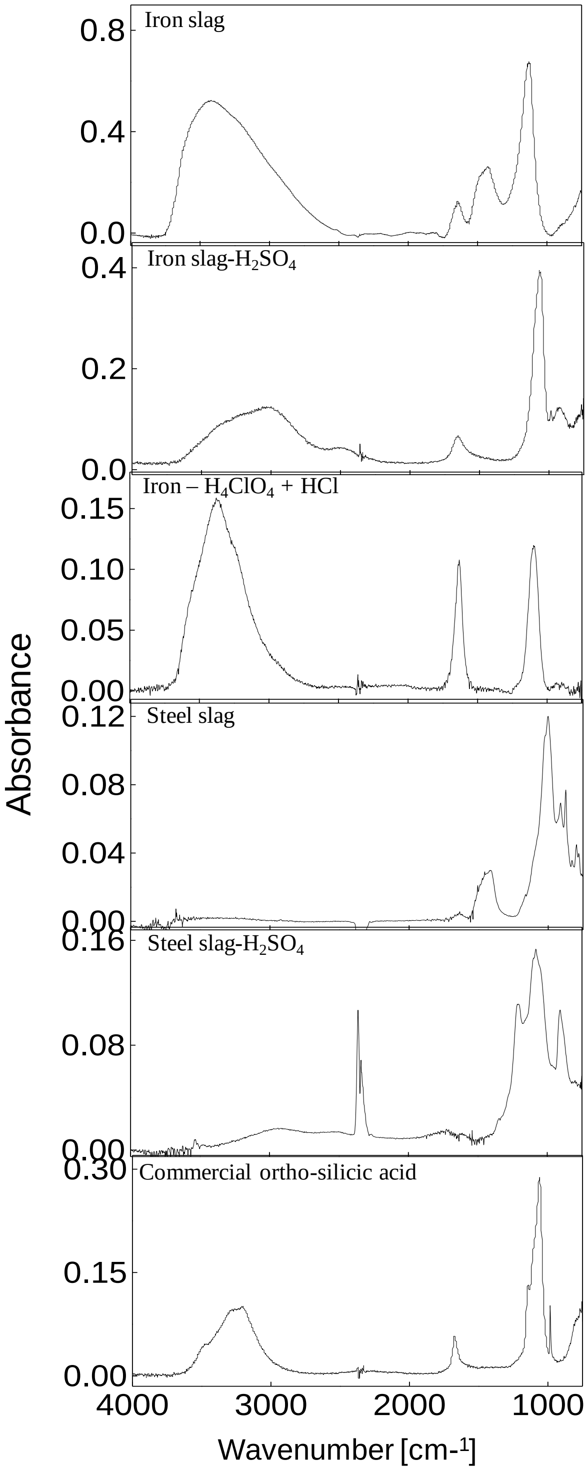

Figure - 2: ATR FT-IR spectra in frequency range of 4000-750 cm^{-1} of iron slag and steel slag before and after acid hydrolysis and commercial ortho-silicic acid.

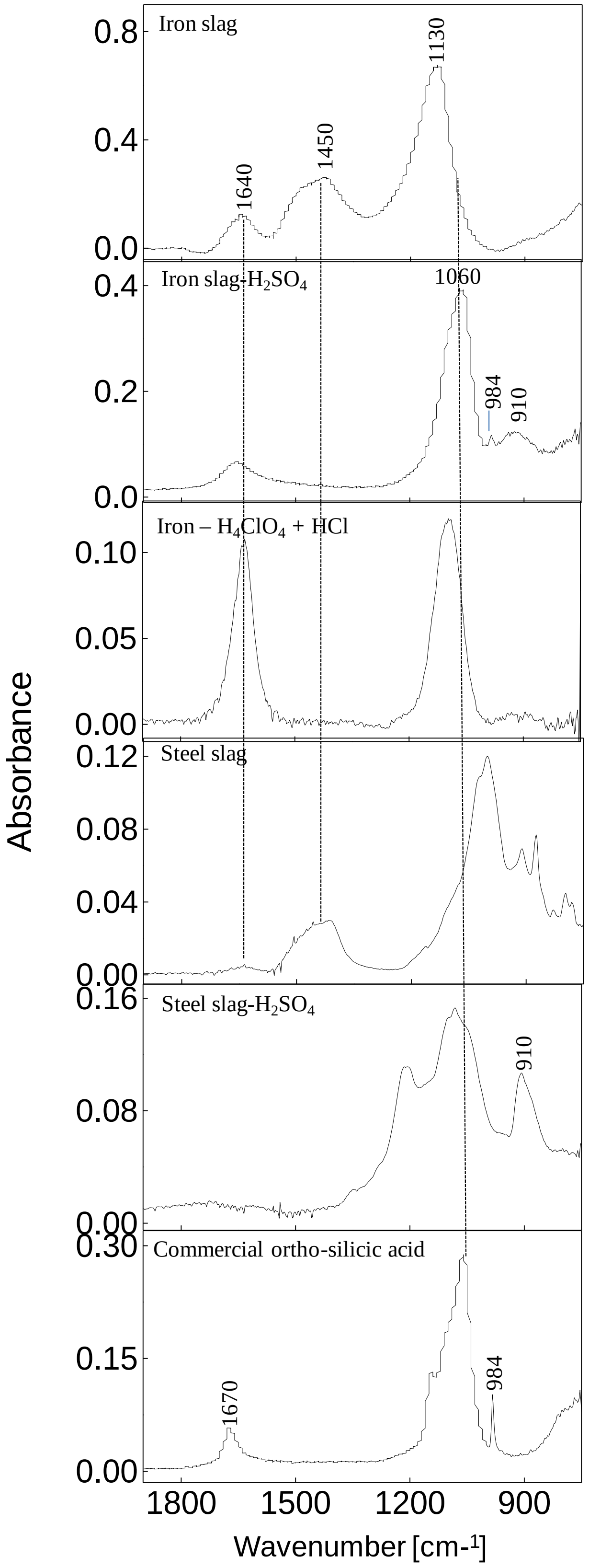
Absorbance
Iron slag
0.8
0.4
0.0
1130
1450
1640
Iron slag-H_2SO_4
0.4
0.2
0.0
1060
984
910
Iron – H_4ClO_4 + HCl
0.10
0.05
0.00
Steel slag
0.12
0.08
0.04
0.00
Steel slag-H_2SO_4
0.16
0.08
0.00
910
Commercial ortho-silicic acid
0.30
0.15
0.00
1670
984
1800
1500
1200
900
Wavenumber [cm-1]

Figure - 3: ATR FT-IR spectra in frequency range of 1900-750 cm^{-1} of iron slag and steel slag before and after acid hydrolysis and commercial ortho-silicic acid.

Table II: Solubility of active silicon extracted from iron slag, steel slag and commercial ortho-silicic acid determined by ICP-OES method.

	Soluble active silicon (%wt.)		
	iron slag	steel slag	commercial ortho-silicic acid
without treatment*	14	11	7.4
H_2SO_4	5.6	3	
H_2O	0.03	0.01	5.4

**The values obtained by means of XRF method.*

Table III: Composition of iron slag before and after acid hydrolysis using H_2SO_4, and commercial ortho-silicic acid determined by XRF method

components	Iron slag	Iron slag after acid hydrolysis	commercial ortho-silicic acid
F	0.58	0.27	26
Na	0.19	0.17	8
Mg	3.73	2.82	10
Al	7.67	4.38	0.03
Si	13.78	6.68	7.41
S	0.79	17.49	11
Cl	0.02		0.04
K	0.8	0.46	0.02
Ca	22.85	0.5	0.03
Ti	0.27	0.14	-
Mn	0.2	0.11	4.89
Fe	0.71	0.34	0.56

5. CONCLUSION

Ortho-silicic acid system, an active soluble form of silica, has been productive by acid hydrolysis of iron slag and steel slag with H_2SO_4. The slags appear to be a promising and extensive source of silicon using as fertilizer. Acid hydrolysis conditions are found to be proportional to extractability of active silicon, whereas the conditions can be further optimized to achieve a superior volume of soluble silicon.

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