

2 METHOD OF STUDY

2.1 Materials

- 2.1.1 Concentrated ilmenite was obtained from the Office of Mineral Resources Region 1, Songkla, Thailand. In appearance it is like black sand and was used in experiment as received without any further modification. The compositions of this ore sample are given in Table 14 (page 67.).
- 2.1.2 Hydrochloric acid 37 %, HCl, A.R., Merck.
- 2.1.3 Sodium chloride, NaCl, A.R., Merck.
- 2.1.4 Hydrogen peroxide 40 % w/v, H₂O₂, code no. 307701005, Carlo Erba.
- 2.1.5 Corn starch 100 %, CPC/Aji, Thailand. The starch used as a binding agent for pressing the specimens into pellet disk.
- 2.1.6 Filter papers No.1, Qualitative, Whatman, England.
- 2.1.7 Universal indicator, full range pH 1 – 14, Whatman, England

2.2 Equipment

- 2.2.1 Sintered glass, beaker 50 mL, soxhlet unit 55/50, three-necked round bottom flask, and condenser were assembled as the leaching reactor.
- 2.2.2 Heating mantle
- 2.2.3 High-temperature beaded heater
- 2.2.4 Thermocouple, Super
- 2.2.5 Orbital shaker, INFORS AG Rittergasse 27 CH-4103 Bottmingen.
- 2.2.6 Die 32 mm in diameter, SPECAC, Kent, UK.
- 2.2.7 Hydraulic press, Ring Press 00-25, Research and Industrial Instruments Co.

- 2.2.8 Analytical balances, AE 200S, SNR M10802, Mettler Toledo A.G., Switzerland.
- 2.2.9 Oven, National, Heinicke Company, U.S.A.
- 2.2.10 pH meter, model 8519, HANNA Instruments, U.S.A
- 2.2.11 pH electrode, model 300731.1 with wetting cap removed, Denver Instrument Company.
- 2.2.12 Low temperature circulator cooling aspirator, CA1111, EYELA, Tokyo Rikakikai Co., Ltd.
- 2.2.13 Energy dispersive x-ray fluorescence, EDXRF, Spectrace 5000, Spectrace Instruments, Inc., Mountainview, California, U.S.A.
- 2.2.14 X-ray diffractometer, XRD, PHILIPS X'Pert MPD, Co tube, at the Scientific Equipment Center, PSU
- 2.2.15 X-ray fluorescence spectrometry, PW2400, Philips Analytical x-ray B.V., Eindhoven, Netherlands, at the Scientific Equipment Center, PSU

2.3 Methods

2.3.1 Several methods to upgrade ilmenite ore

Several methods to upgrade ilmenite ore were studied in this work as follows.

2.3.1.1 Main procedure (Method A)

Ilmenite ore was placed in the sintered glass. This sintered glass was then placed in a 50 mL beaker which in turn was placed in a soxhlet unit (Figure 4). Concentrated hydrochloric acid was added to fill up the sintered glass in the soxhlet. The soxhlet was fitted with a condenser and joined to a three-necked round bottom flask containing 600 mL of concentrated hydrochloric acid. (The condenser

was fed with cold water, 5°C.) The other two necks of round bottom flask were fitted with air pump (for flowing air bubbles to reduce bumping) and a thermometer. The heating was provided to round bottom flask by a heating mantle and at the soxhlet by high-temperature beaded heater that used a thermocouple to control temperature. Figures 5 and 6 are sketches showing the reactor set up in this section (Method A). At the beginning of the leaching the solution in the soxhlet was brownish yellow and at the end of the leaching the solution in soxhlet turned to colorless. After that the residue was filtered and washed with water until the washing was free of acid. The residue was dried in the oven at 105°C and analyzed by Energy Dispersive X-Ray Fluorescence spectrometry(EDXRF).

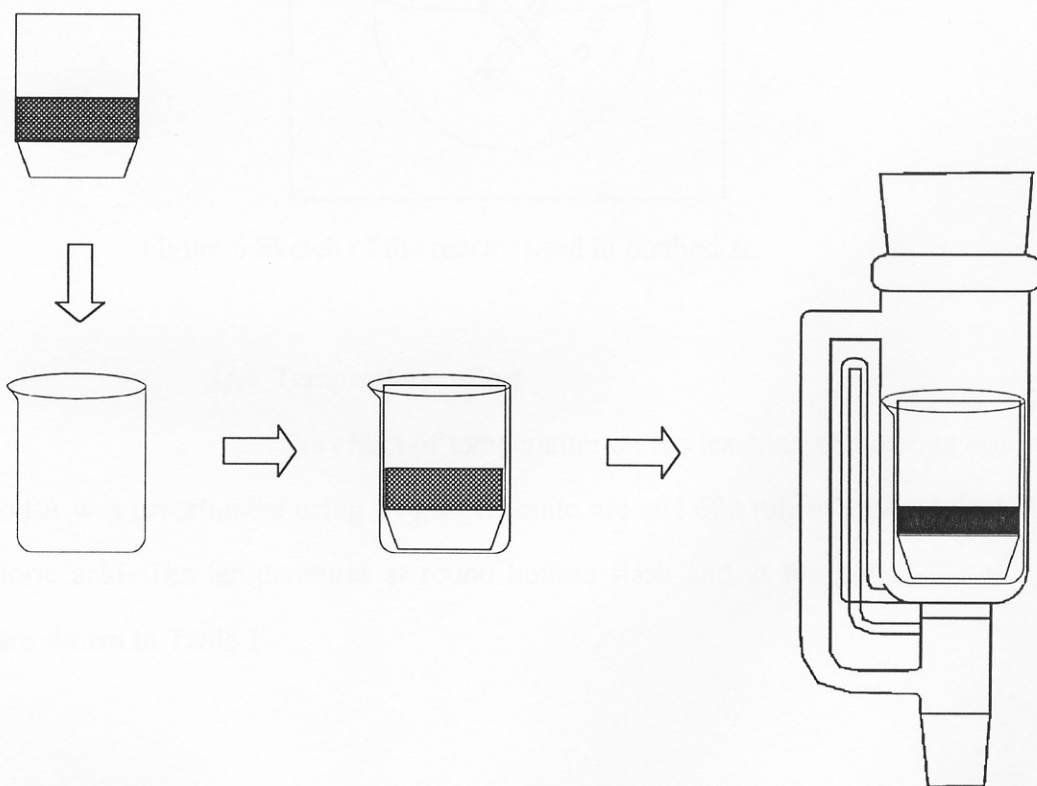


Figure 5 Sketch of set up in the soxhlet section in method A.

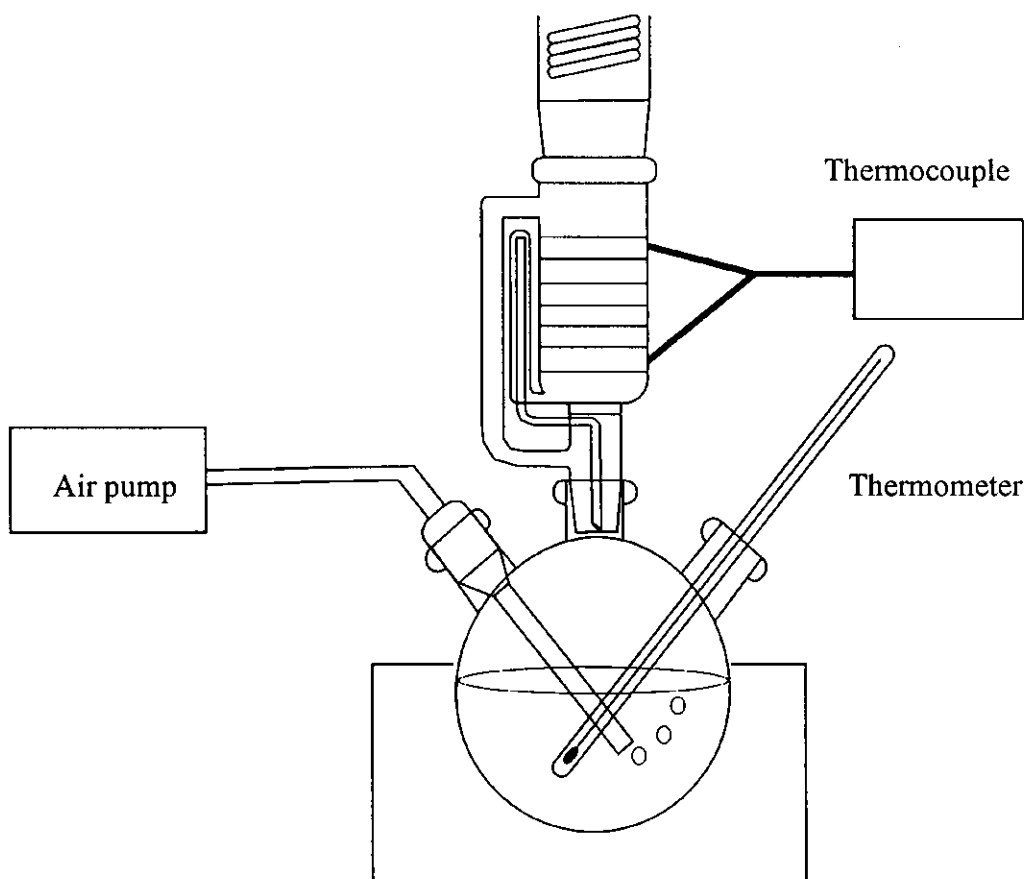


Figure 6 Sketch of the reactor used in method A.

(A) Temperature effect

The effect of temperature on the leaching of ilmenite ore by method A was investigated using 15 g of ilmenite ore and 600 mL of concentrated hydrochloric acid. The temperatures at round bottom flask and at the outer side of soxhlet are shown in Table 1.

Table 1. Temperature at round bottom flask and outer side of soxhlet

No.	temperature at round bottom flask($^{\circ}$ C)	temperature at outer side of soxhlet($^{\circ}$ C)
1	93	80
2	97	80
3	97	120
4	105	120

(B) Ratio of ilmenite ore to acid

The effect of initial ilmenite ore to acid ratio on the leaching by method A was investigated in 600 mL of concentrated hydrochloric acid and temperature of round bottom flask and soxhlet at 105 and 120 $^{\circ}$ C, respectively. The amounts of ilmenite ore were 5, 10, and 15 g.

2.3.1.2 NaCl effect (method B)

The effect of NaCl on the leaching by hydrochloric acid was investigated in two different routes.

(A) Method B1

Ilmenite ore, about 15 g, was mixed with NaCl, 5-15 g, in sintered glass and subjected to leaching by the same set up as method A. The mixing with NaCl was to increase Cl^- to react with Fe^{3+} in ilmenite ore.

(B) Method B2

NaCl (15 g) was added into 600 mL of concentrated hydrochloric acid in round bottom flask and used this mixture as leachant to leach ilmenite ore, 15 g, by the same set up as method A.

2.3.1.3 H₂O₂ effect (method C)

The effect of H₂O₂ on the leaching was investigated using the same set up as method A for 65 hours. After filtration the residue was infused in H₂O₂ 40 % w/v for 24 hours to oxidized Fe²⁺ that remained in the ore. The residue was filtered and leached again by the same set up as method A.

2.3.1.4 Method D

Method D was to study the combined effect of NaCl and H₂O₂. The investigation of this method was carried out in two different ways.

(A) Method D1

Ilmenite ore, about 15 g, was mixed with NaCl, 10 g, in sintered glass and subjected to leaching by the same set up as method A for about 48 hours, after the filtration the residue was infused in H₂O₂ 40 % for 24 hours. The residue was filtered and leached again by the same set up for 48 hours.

(B) Method D2

Ilmenite ore was leached by the same set up as method A for 50 hours, after the filtration the residue was infused in H₂O₂ 40 % for 24 hours. The residue was filtered and leached again by the same set up as method A for 48 hours. The leachant in this case contained 10 g of NaCl.

2.3.1.5 Method E

Ilmenite ore, about 15 g, was placed in the modified sintered glass having long stem with the draining hole 1 inch from the top as shown in Figure 7. Sintered glass was placed in three-necked round bottom flask and 600 ml of concentrated hydrochloric acid was added to sintered glass in the round bottom flask. Then fitted a condenser to the round bottom flask. The other two necks of round bottom flask were fitted with air pump and a thermometer. The heating was provided to round bottom flask by heating mantle as shown in Figure 8. After that the residue was filtered and washed with water until the washing was free of acid. The residue was dried in the oven at 105°C.

2.3.1.6 Double leaching with fresh acid

The ore was leached twice, each time with fresh acid. Two methods were investigated as follows.

(A) Using residue from method A (method AA)

Ilmenite ore was leached by method A for 65 hours, after the filtration the residue was leached again by the same set up with new fresh concentrated hydrochloric acid for 24 hours (the solution in soxhlet turned to colorless).

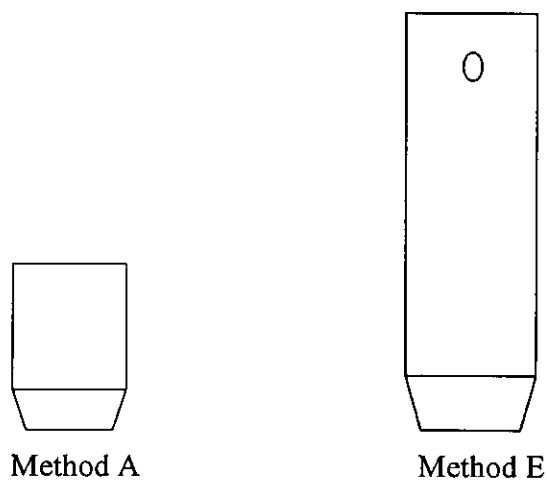


Figure 7 Sketch of the sintered glasses used in method A and method E.

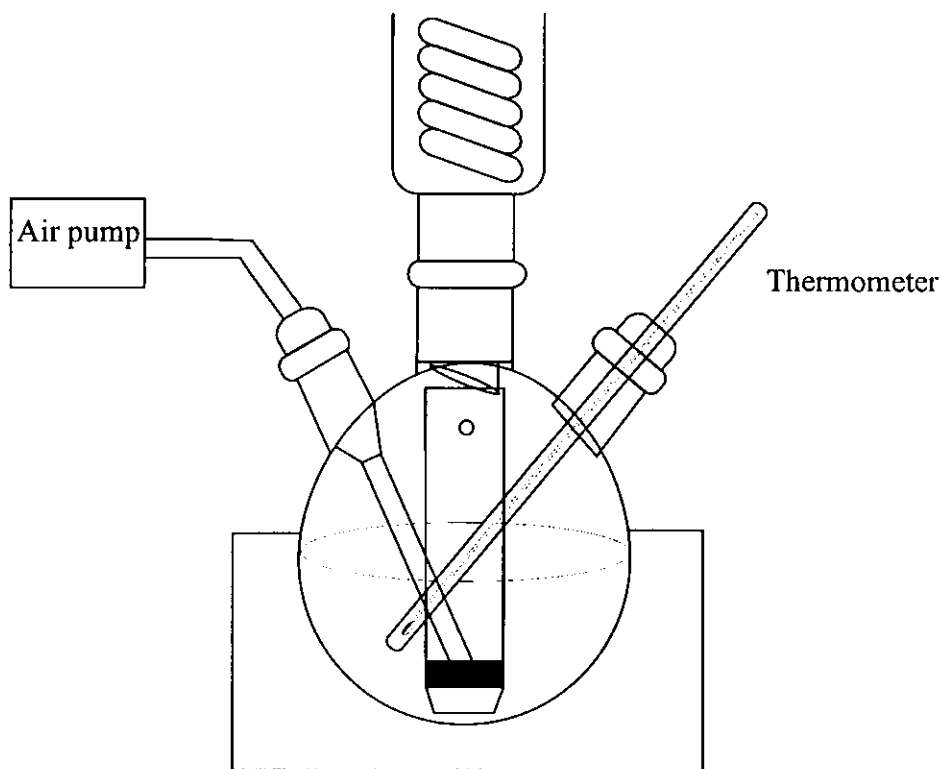


Figure 8 Sketch of the reactor used in method E.

(B) Using residue from method C (method CA)

Ilmenite ore was leached by the same set up as method A for 65 hours, after the filtration the residue was infused in 30 mL of H₂O₂ 40 % w/v for 24 hours (method C). The residue was filtered and leached again by the same set up as method A with new fresh concentrated hydrochloric acid for 24 hours.

2.3.1.7 Method F

The method F was similar to method A but did not use the air pump for flowing air bubbles to reduce bumping. All the details were the same as described in 2.3.1.1 (method A).

Since at the same set up as method A was used but, this method showed different results, so the effect of temperature of leachant in round bottom flask, temperature at the outer side of soxhlet, initial ratio of ore to acid, and leaching time was studied.

(A) Temperature of leachant in round bottom flask

The effect of temperature of leachant in round bottom flask on the leaching by method F was investigated using 15 g of ilmenite ore and 600 mL of concentrated hydrochloric acid. In each case, the temperature of leachant in round bottom flask was 98°C and 112 °C and temperature at the outer side of soxhlet was 120°C. After leaching for 24 hours the amount of Fe and Mn remained in the residues were determined with wavelength dispersive x-ray fluorescence (WDXRF) spectrometer.

(B) Temperature at the outer side of soxhlet

The effect of temperature at soxhlet* on the leaching by method F was investigated using 15 g of ilmenite ore and 600 ml of concentrated hydrochloric acid. The temperature of leachant in round bottom flask was 112°C and temperatures at the soxhlet* were 90, 100, 110, 120, and 130°C. After leaching for 24 hours and the amount of Fe and Mn remained in the residues were determined with WDXRF.

(C) Initial ratio of ilmenite ore to acid

The effect of initial ilmenite ore to acid ratio on the leaching by method F was investigated in 600 ml of concentrated hydrochloric acid and temperature of the leachant in round bottom flask and the soxhlet at 112 and 120°C, respectively. The amount of ilmenite ore were 10, 15, and 20 g. After leaching for 24 hrs the amount of Fe and Mn remained in the residues were determined with WDXRF.

(D) Leaching time

The effect of leaching time on the leaching by method F was investigated by using 15 g of ilmenite ore and 600 ml of concentrated hydrochloric acid. In each case, temperature of the leachant in round bottom flask and the soxhlet at 112 and 120°C, respectively. After leaching for 12, 17, 24, and 30 hours the amount of Fe and Mn remained in the residues were determined with WDXRF.

2.3.2 Measurement of temperature at the soxhlet

Since the temperature at the soxhlet could not be measured directly by using thermometer so, this experiment needs to be carried out. Two methods were used in this study.

* measured at the out side of soxhlet

2.3.2.1 Sintered glass containing 30 mL water was placed in 50 mL beaker which in turn was placed in soxhlet unit. The soxhlet was joined to two-necked round bottom flask containing 600 mL water. The other neck of round bottom flask was fitted with thermometer. The heating was provided to round bottom flask by heating mantle until the water boiled (100°C) and heat the soxhlet by high-temperature beaded heater that use thermocouple to control temperature. Set the soxhlet temperatures at 100, 110, 120, 130, and 140°C . The water temperature in soxhlet was measured by thermometer until it was constant at each temperature set. Figure 9 (a) was shown the reactor set up in measurement of temperature at soxhlet.

2.2.3.2 The set up was the same but the top of soxhlet was covered with beaker as shown in Figure 9(b).

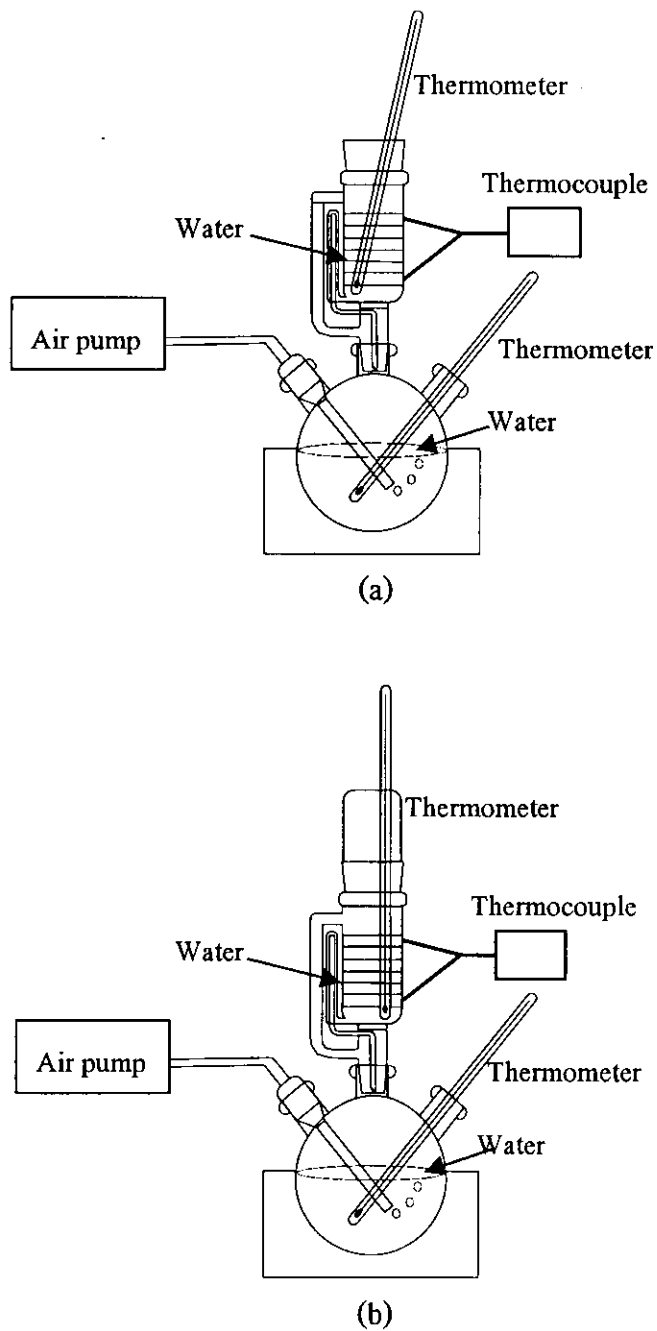


Figure 9 Sketch of reactor used in measurement of temperature at the soxhlet experiment (a) no cover on the soxhlet (2.3.2.1), (b) covered the soxhlet with beaker (2.3.2.2).

2.3.3 Determination of acid concentration

In order to follow the acidity change during the leaching process more experiments need to be carried out. First, the concentration of fresh concentrated hydrochloric acid was determined. Then the blank experiment was set up as in method A without the mineral. In this experiment the acid was refluxed for 2 hours and sample of acid was drawn for the titration and the rest was allowed to reflux to 65 hours for method A and 24 hours for method F and the acid was aliquoted for another titration. Another experiment was set up as in method A with ilmenite added. Aliquots of acid were drawn for titration at 2 hours and 65 hours for method A and 24 hours for method F as in the first experiment.

The method to determine acid concentration was as follows. Diluted sample solution to proper concentration, then titrated with standard solution NaOH 1 by 1 mL and the pH was measured. The end point was obtained from the resulting titration plot.

2.3.4 Quantitative analysis by energy dispersive x-ray fluorescence (EDXRF)

The compositions of the starting ilmenite ore and the residue after leaching were carried out using an EDXRF. Ilmenite ore itself is only partially soluble in acid and the residue is insoluble part of the ore. The advantages of XRF in comparison with wet chemical methods are the accurate analysis of mineralogical samples which are difficult to dissolve. The energy dispersive x-ray fluorescence (EDXRF) spectrometer (Spectrace 5000, Spectrace Instruments, Inc., Mountainview, California) is of the tube type. The excitation x-ray is generated from a tube using a Rh target. The detector is Si(Li) with resolution of 164 eV for the Mn $K\alpha$ line. This spectrometer is fully computerized and controlled by the software EDXRF version 1.35.

2.3.5 X-ray powder diffraction patterns (XRD)

The XRD spectra were obtained through the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla, using an x-ray diffractometer, X'Pert MPD, Co tube, Philips.

2.3.6 Quantitative analysis by wavelength dispersive x-ray fluorescence (WDXRF)

This technique was used to determine the amounts Fe, Mn, W, Sn, Nb, Zr and Y that were present in both starting ilmenite ore and the residue after leaching. The linear calibration curve of each element was used for the analysis. All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla, using a PW2400, Philips Analytical x-ray B.V., Eindhoven, Netherlands.

2.3.6.1 Calibration standards

Calibration standards at three different concentrations for each element (Fe, Mn, W, Sn, Nb, Zr, and Y) were used for linear curve plots. All of the calibration standard pellets were the same set as used by Wongnawa, *et al.* (1997). The concentrations of the standards were given in Table 2.

2.3.6.2 Preparation of the ore specimens

Each ore sample was finely ground before mixing with corn starch in the ratio 1/5 (ore/starch, w/w) in 250 mL Erlenmeyer flask. Three or four pieces of clear plastic and carbolite blocks were put into the flask to act as moving stirrers. The flask content was shaken on the lab shaker at 280 rpm for 24 hours to ensure homogeneity. After shaking, samples (weighing exactly 4 g each) of the mixed powder were pressed as pellet disk of 32 mm diameter under a pressure of 8 tons per square inch. The pellet thus obtained was considered as infinitely thick.

Table 2 The concentration of each element in the standard pellets.

element	Concentration (%)		
	1	2	3
Fe	0.21	1.01	1.80
Mn	0.03	0.10	0.18
W	0.51	0.66	1.02
Sn	0.42	0.84	1.28
Nb	0.15	0.22	0.26
Zr	0.12	0.19	0.31
Y (ppm)	799.93	1220.28	1600.39