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Application of thermal techniques in the recovery of heavy minerals from oil-sand tailings

Shaheer A. Mikhail*, Anne-Marie Turcotte, Colin A. Hamer

Mineral Sciences Laboratories, Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Ont. K1A 0G1, Canada

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Abstract

Thermal techniques, namely, thermogravimetry (TG), simultaneous thermogravimetry–differential thermal analysis–Fourier transform infrared spectroscopy (TG–DTA–FTIR) and thermomagnetometry, were used to examine the thermal behaviour of heavy-mineral tailings generated in oil-sand steam processing operations. The results will be used in the selection and optimization of a thermal process to remove residual bitumen in the tailings and recover the contained titanium and zirconium values. The recovery of heavy minerals from the tailings would contribute significantly to the environmental sustainability as well as to the commercial viability of the operations. The results of the study indicated that the residual bitumen can be removed by heating the material in an oxidizing atmosphere at about 600°C. The product may then be heated to a higher temperature in a reducing atmosphere to decompose the complex titanium/iron minerals and later recover titanium values by separating the iron or iron oxide magnetically.

Keywords: Bitumen; Heavy minerals; Oil-sand processing; TG–DTA–FTIR; Thermomagnetometry; X-ray diffraction

1. Introduction

Titanium and zirconium minerals are abundant throughout the oil-sand deposits of Western Canada. These deposits are presently being exploited by large mining companies who treat about 200 Mt of oil-sands per annum for the extraction of over 120 M bbl of bitumen. The extraction process involves an initial treatment of the sand with steam for the extraction of crude bitumen which is subsequently mixed with

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* Corresponding author.

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a frother and centrifuged to remove entrained solids. The process generates a tailings stream containing significant amounts of heavy minerals. An estimated 2.7 Mt a^{-1} of tailings containing 8–12% TiO_2 and 2–4% ZrO_2 are generated.

A project has been undertaken by Canada Centre for Mineral and Energy Technology to determine the technical and economic feasibility of recovering heavy minerals from the oil-sands tailings. The first stage involved the concentration of the bitumen-containing heavy minerals by flotation. The concentrate would then be roasted to remove the bitumen. The roast would subsequently be treated by mineral processing techniques, such as magnetic, gravity and electrostatic operations, to produce concentrates of titanium-and zirconium-bearing minerals. The titanium-bearing concentrates of ilmenite, leucoxene and rutile may be further upgraded, by reduction or other means, to synthetic rutile.

In the present work, the determination of the thermal and thermomagnetic behaviour of the oil-sand tailings concentrate was carried out using thermal analysis, Fourier transform infrared spectroscopy and thermomagnetometry to determine optimum conditions for the thermal treatment of the concentrate and for potential treatment of the roast by reduction.

2. Experimental

An industrial sample of oil-sand tailings concentrate containing residual bitumen was subjected to column flotation in order to concentrate the heavy minerals and was then dried at 110°C. A representative sample of the flotation concentrate, still containing the residual bitumen, was used in this study. Mineralogical and X-ray diffraction (XRD) analyses indicated that the sample contained rutile (TiO_2), leucoxene ($Fe_xTi_yO_z$), zircon ($ZrSiO_4$), complex silicates, siderite ($FeCO_3$), pyrite (FeS_2), ilmenite ($FeTiO_3$) and other minor and trace components.

The thermal analysis (TA) measurements were carried out using a Seiko SSC5200H–TG–DTA 320 instrument. The identification of the evolved gaseous species was performed using a BOMEM-MB100 Fourier transform infrared (FTIR) spectrometer interfaced and used simultaneously with the thermal analyzer. Samples of about 20 mg each ($< 100\,\mu m$ particle size) were heated in the thermal analyzer at 20°C min^{-1} in a selected atmosphere with a flow rate of 150 ml min^{-1}. The acquired TA and FTIR data were transferred to an external computer for plotting using Sigma Plot or Spectra Calc software. The thermomagnetometry measurements were also obtained using the Seiko instrument, modified with an external magnet. Thermomagnetometry is a modern method for detecting magnetic materials by means of detecting their magnetic transitions (Curie point). The principle and procedure of thermomagnetometry were reported earlier [1].

3. Results and discussion

At the early stages of the study, the thermal behaviour of the material was examined in an inert atmosphere. The results are presented in Fig. 1 in terms of TG–DTA curves

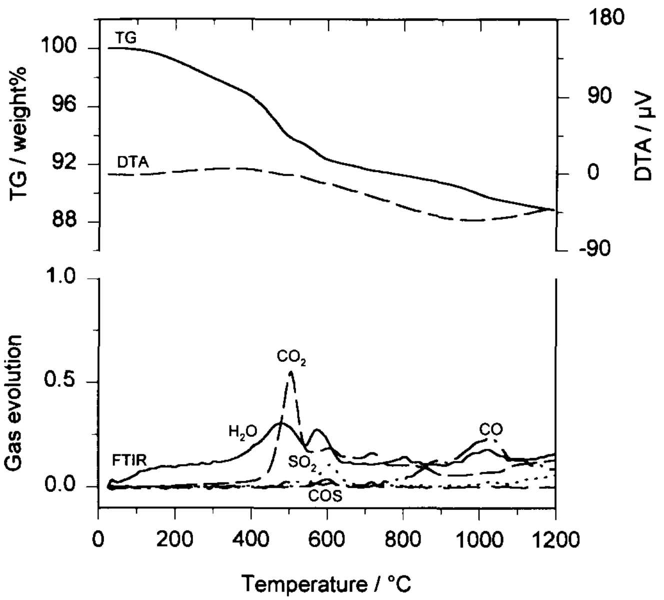

Fig. 1. TG–DTA–FTIR diagram for the flotation concentrate in N_2.

together with corresponding FTIR gas-evolution curves. As can be seen from the weight-loss curve (TG) and the gas-evolution profiles, most of the activities occur in the temperature range 350–650°C. The gradual weight loss throughout most of the temperature range and the release of gases such as CO_2, H_2O, CO, COS and SO_2, primarily in the temperature range 350–650°C, are typical of the pyrolysis of tars [2]. The higher weight loss in this temperature range is also due to the decomposition of pyrite and siderite contained in the sample, according to the following reactions:

$$FeS_2 = \frac{1}{1-x} Fe_{1-x}S + \frac{1-2x}{2-2x} S_2 \qquad (1)$$

$$FeCO_3 = FeO + CO_2 \qquad (2)$$

The products of reaction 2 may further react to form Fe_3O_4 and CO [3]. A total weight loss of about 11% was observed at 1200°C. No detectable thermal activity was observed by DTA, however, because of the absence of any significant oxidizing atmosphere.

Fig. 2 represents the TG–DTA–FTIR curves obtained on heating the sample in air. Although the total weight loss was similar to that determined when the sample was heated in inert atmosphere, a higher proportion of the weight loss occurred at 350–650°C. Corresponding exothermic activity also appeared on the DTA curve signifying the combustion of bitumen, the decomposition of siderite according to reaction 2 and the oxidation of pyrite according to the following general reaction:

$$2FeS_2 + 5\tfrac{1}{2}O_2 = Fe_2O_3 + 4SO_2 \qquad (3)$$

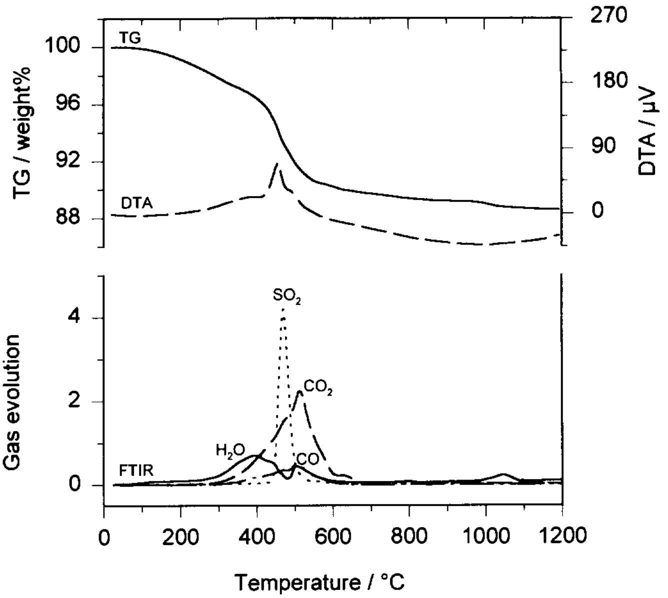

Fig. 2. TG–DTA–FTIR diagram for the flotation concentrate in air.

The shape of the exothermic trend on the DTA curve is typical for the oxidation of pyrite [4]. Reaction 3 is also verified by the significant increase in SO_2 evolution as shown on the gas-evolution curves (notice the different scale). A small weight loss, accompanied by an H_2O evolution trend around 1000°C may be due to the loss of structural water from contained complex silicates.

The material was also examined in a reducing atmosphere ($20\%H_2$–$80\%N_2$), Fig. 3. As expected, the trend of the weight change is similar to that detected in an inert atmosphere up to about 700°C. Above this temperature, however, a higher weight loss took place with a final weight loss at 1200°C of 17%, indicating that a reduction of contained oxides has taken place. This is verified by the substantial increase in H_2O evolution (FTIR gas-evolution curves) throughout the whole temperature range. Traces of CH_4 gas were also detected, which can be related to the evolution of bitumen volatiles in a reducing atmosphere. Although not included on the gas-evolution curves, H_2S is also expected to be present as a product of the decomposition of pyrite in H_2 according to the following reaction:

$$FeS_2 + H_2 = FeS + H_2S \tag{4}$$

The FTIR absorption bands of H_2S, however, are most difficult to resolve since they overlap with those of H_2O, CO_2 and CH_4 [5]; no attempts have been made to measure H_2S evolution. The DTA curve in Fig. 3 is also similar to that obtained in inert atmosphere with no detectable thermal effects.

The concentrate was also examined by thermomagnetometry to determine if it could be rendered magnetic or partially magnetic when treated thermally in a reducing

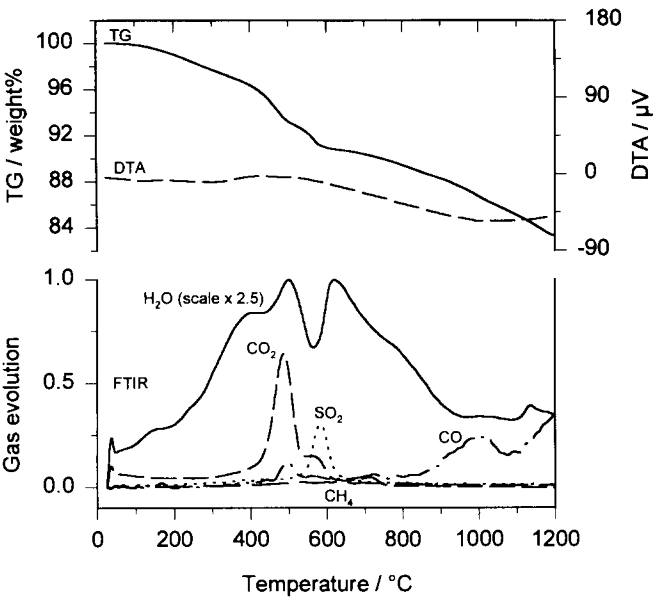

Fig. 3. TG–DTA–FTIR diagram for the floation concentrate in a 20% H_2–80% N_2 atmosphere.

atmosphere. Thermomagnetometry is essentially thermogravimetry with the capability to detect the magnetic transformation from the ferri or ferromagnetic form to the paramagnetic one (Curie temperature) or vice versa. It is, therefore, a sensitive method for detecting the presence of—and identifying—magnetic components in a complex material such as the flotation concentrate. Fig. 4 shows the weight loss curves of the concentrate as heated up to 1000°C in different reducing atmosphere, namely, H_2–N_2, CO–CO_2 and CH_4–N_2 as well as mixed with solid carbon in N_2. The extent of weight loss in the present context is directly related to the extent of reduction of contained oxides in a specific atmosphere. Hence, it is evident from Fig. 4 that the reduction is relatively most extensive in the H_2–N_2 atmosphere above 450°C. It must be realized, however, that only the gas (and carbon/concentrate) ratios shown in Fig. 4 were examined. Fig. 5 shows the cooling curves of the same experiments, maintaining the same reducing atmospheres used on heating. An apparent weight loss at 770°C detected by thermomagnetometry on the curve obtained in H_2–N_2 indicated the presence of metallic iron (Curie temperature is 770°C [6]) in the sample. A very small shift in the baseline around 575°C on the curve obtained with the carbon mixture indicated the presence of magnetite (Curie temperature is 595°C [6]).

A batch of flotation concentrate was heated to 650°C in air to remove the contained bitumen and convert the contained pyrite and siderite to iron oxide. X-ray diffraction of this roast indicated the presence of rutile, zircon, ilmenite, haematite, silica and leucoxene. The thermal behaviour of this roast was then examined with the same reducing agents used with the concentrate, Fig. 6. It can be seen that the reduction reactions start at different temperatures and proceed with different trends, depending

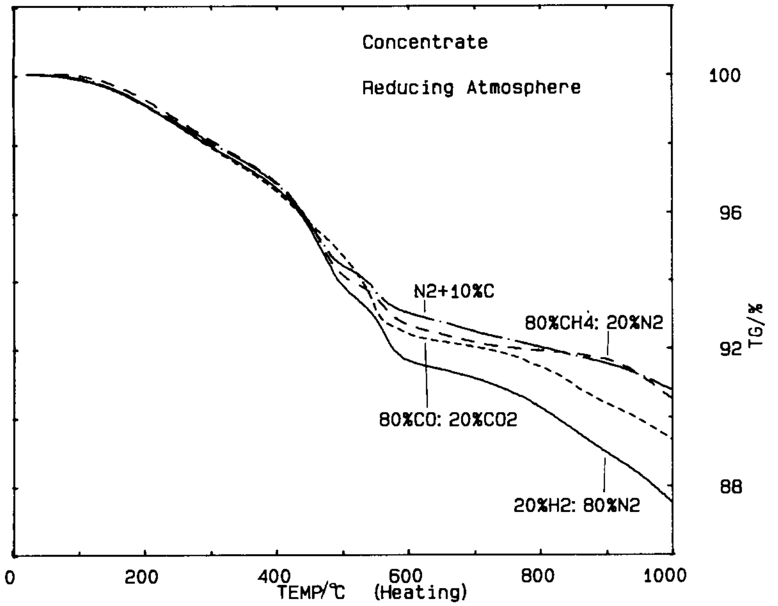

Fig. 4. TG curves for the flotation concentrate in different reducing atmosphere.

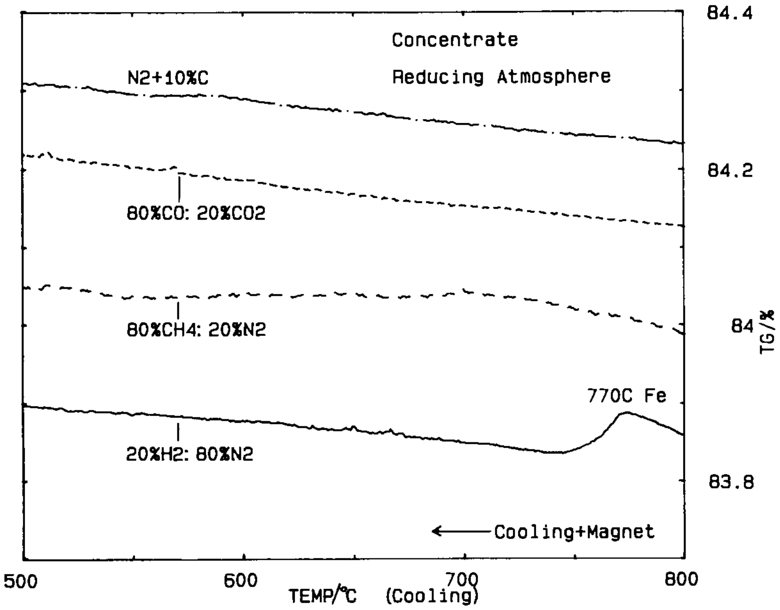

Fig. 5. TM cooling curves for the flotation concentrate in different reducing atmospheres.

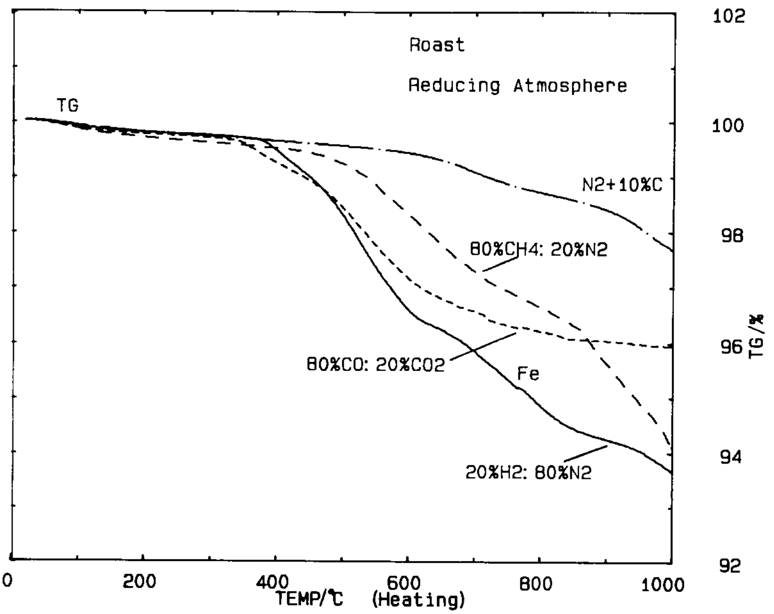

Fig. 6. TG curves for the roast in different reducing atmospheres.

on the reducing agent. Similar to the reduction of the concentrate, the H_2/N_2 atmosphere seems to be the most effective. Cooling curves of the same experiments, obtained under the same reducing atmospheres used on heating, are shown in Fig. 7. An apparent weight loss at 770°C detected by thermomagnetometry on the curves obtained in H_2/N_2 and in CO/CO_2 indicated the presence of metallic iron in the sample. With the carbon mixture, the apparent weight loss is evident at 575°C, indicative of the presence of magnetite. In the CH_4–N_2 atmosphere, the apparent weight loss appeared around 700°C, which may indicate the presence of iron carbide. These results indicate that the reduction of the roast can be achieved using different reductants with the formation of different magnetic products. The extent of reduction and the amount of the magnetic product are also dependent on the reducing agent.

In separate experiments using H_2–N_2 as a reductant for the roast, heating was interrupted at preselected temperatures and the product was examined by XRD. At 625°C, the product contained minor amounts of magnetite and metallic iron, together with the major components, rutile, zircon, ilmenite, silica and leucoxene. Magnetite and metallic iron seem to have formed as a result of the reduction of haematite, a significant component in the roast. At 900°C and at 1000°C, XRD indicated the presence of metallic iron together with rutile, zircon and silica and the disappearance of ilmenite and leucoxene (although leucoxene was not detected by XRD (limit of detection is 5–6%), the mineralogical analysis indicated the presence of significant amounts; a point which requires further investigation). These results indicated that haematite can be converted to magnetite and/or metallic iron by heating the roast to 625°C in H_2–N_2

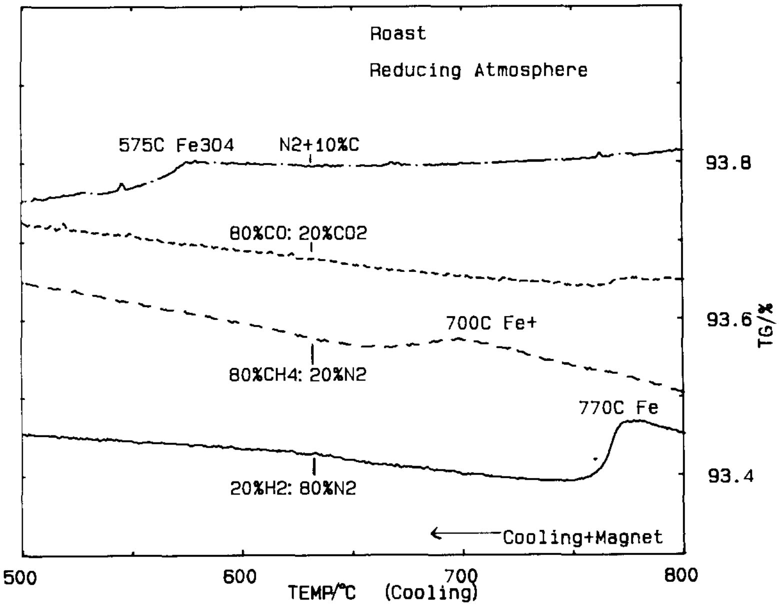

Fig. 7. TM cooling curves for the roast in different reducing atmospheres.

atmosphere. Contained iron/titanium compounds like ilmenite and leucoxene may also decompose, at least partially, to rutile, magnetite and/or metallic iron at higher temperatures.

Based on these results, a process is proposed in which the flotation concentrate is roasted at 650°C to remove contained bitumen and to convert pyrite and siderite into haematite. The roast may then be subjected to reduction at a higher temperature (900–1000°C) to convert the haematite into magnetite and/or metallic iron and decompose the complex titanium and/or iron compounds. The final product would then be processed magnetically to remove the ferrous and other magnetic components and recover the heavy metal values. Physical processing may also be used to concentrate the haematite and complex titanium and/or iron compounds in the roast before subjecting it to reduction.

4. Conclusions

The thermal behaviour of a flotation concentrate of heavy-mineral tailings from oil-sand operations was studied using TG, TG–DTA–FTIR and TM. The results indicated that contained bitumen residues can be removed from the concentrate by heating to 650°C in flowing air. During this step, contained pyrite and siderite oxidize to form haematite. The produced roast was examined in different reducing atmospheres at higher temperatures. Haematite was found to convert to magnetite and/or metallic iron at or above 625°C. Between 625°C and 900°C, complex iron and/or titanium components seem to decompose, at least partially, to their basic components. An outline of a thermal process for the treatment of the flotation concentrate to recover heavy minerals is proposed.

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