Journal of Thermal Analysis, Vol. 37 (1991) 945-951

PREPARATION AND CHARACTERISATION OF MAGNESIUM SULPHATE HEPTAHYDRATE FROM KIMBERLITE TAILINGS

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(Received May 2, 1990; in revised form August 1, 1990)

Weathered Kimberlite tailings of Panna Diamond Mines were characterised by DTA and XRD techniques. The XRD pattern shows the presence of serpentine, quartz, calcite, hematite, magnetite and anatase phases. DTA curve indicates first endothermic peak at 125°C due to dehydration of the mineral and second endo peak at 670°C due to dehydroxylation of serpentine closely followed by an exothermic peak at 810°C associated with the formation of forsterite. XRD and DTA studies of sulphuric acid leach residue of the Kimberlite shows the disappearance of serpentine phase with the appearance of $CaSO_4 \cdot 2H_2O$ phase. The product $MgSO_4 \cdot 7H_2O$ obtained after purification and crystallisation. From the optical emission spectroscopic analysis, the product was found to contain Ca, Fe and SiO_2 as trace impurities.

About 1.5 to 2.0 million tonnes of weathered Kimberlite tailings containing 22% MgO and 32% SiO_2 are stock piled at Panna Diamond Mines of M/s Mineral Development Corporation Limited. Sahu and Venkatesan [1] reported the use of these tailings for iron ore sintering, preparation of glazed and mosaic floor tiles. Kimberlites are generally ultramafic rocks with a main matrix of serpentine [$Mg_3Si_2O_5(OH)_4$] and phlogophite [$KMg_2(OH)_2$ ($AlSi_3O_{10}$)] with chlorite $\{(Mg,Fe,Al)_6(OH)_8$ $[(Al,Si)_4O_{10}]\}$ and carbonate as subordinate minerals [2–4]. The various leachants reported for the dissolution of magnesium metal values are HCl [5], aqueous SO_2 [6] and H_2SO_4 [7, 8].

The present paper deals with the XRD and TG-DTA techniques employed for the characterisation of the weathered Kimberlite tailings, leach residue and product $MgSO_4 \cdot 7H_2O$ obtained during processing of the Kimberlite by H_2SO_4 leaching.

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Experimental

To carry out XRD, DTA and leaching studies, the sample was ground to −80 mesh BSS. X-ray diffractograms were obtained with Philips automatic powder diffractometer and DTA runs were taken using Netzsch simultaneous STA 409 model instrument. Samples of 175 mg were run at a heating rate of 10 deg/min in platinum crucibles under static air using calcined alumina as reference. 20 g of sample was taken in a conical flask fitted with a thermometer and condenser was leached with sulphuric acid on heater cum magnetic stirrer. The analysis of Mg, Ca and Fe was done by using Perkin Elmer 372 atomic absorption spectrophotometer and SiO_2 by colorimetry. Chemical analysis of Kimberlite indicate 13.62% Mg, 6.67% Ca, 7.34% Fe, 33.0% SiO_2.

Results and discussion

The XRD patterns of the Kimberlite shows the presence of serpentine, quartz, calcite and chlorite as major phases and hematite, magnetite and anatase (TiO_2) as minor phases (Fig. 1). The TG-DTA curve of the sample was indicated in Fig. 2. TG curve shows two major weight loss regions in the

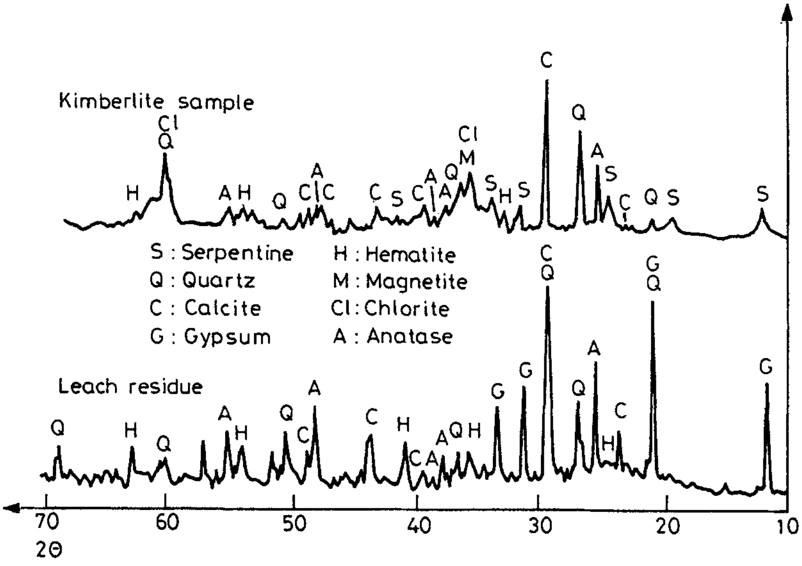

Fig. 1 X-ray diffraction of Kimberlite tailings and H_2SO_4 leach residue

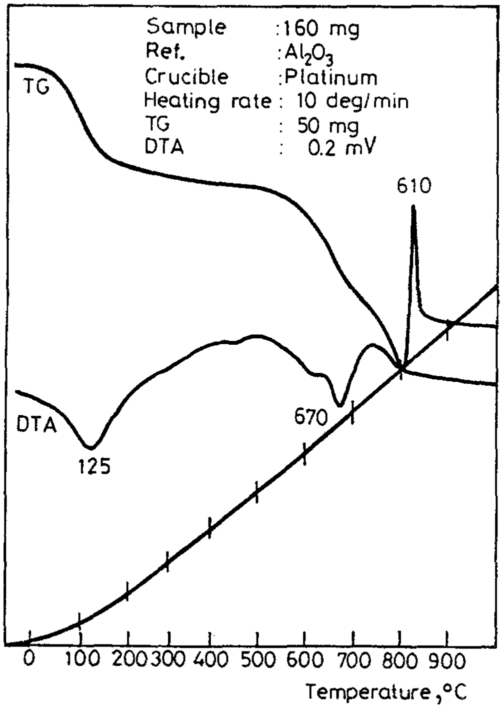

Fig. 2 DTA and TG curve of Kimberlite tailings

temperature ranges of 50 to 250° and 500 to 800° with the corersponding DTA endothermic peaks at 125°and 670° due to the moisture loss and dehydroxylation of the serpentine respectively. Further, the exothermic peak observed at 810° corresponds to the recrystallisation of serpentine leading to the formation of forsterite (Mg_2SiO_4) [9]. Though, the chemical and XRD studies of Kumberlite indicate that there is considerable amount of silica in the Kimberlite tailings, the DTA heating and cooling curve did not show any characteristic quartz peak, indicating that silica is not present in the mineral in free state. The total weight loss observed in the TG curve up to 1000° is 15.6%.

Sulphuric acid leaching of Kimberlite

Leaching of Kimberlite with sulphuric acid results in the formation of $MgSO_4$, $CaSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, H_2SiO_4 and SiO_2 depending on leaching conditions. In the present investigation the leaching of Kimberlite was carried out with 6.2% (v/v) sulphuric acid at 20% pulp density and temperature

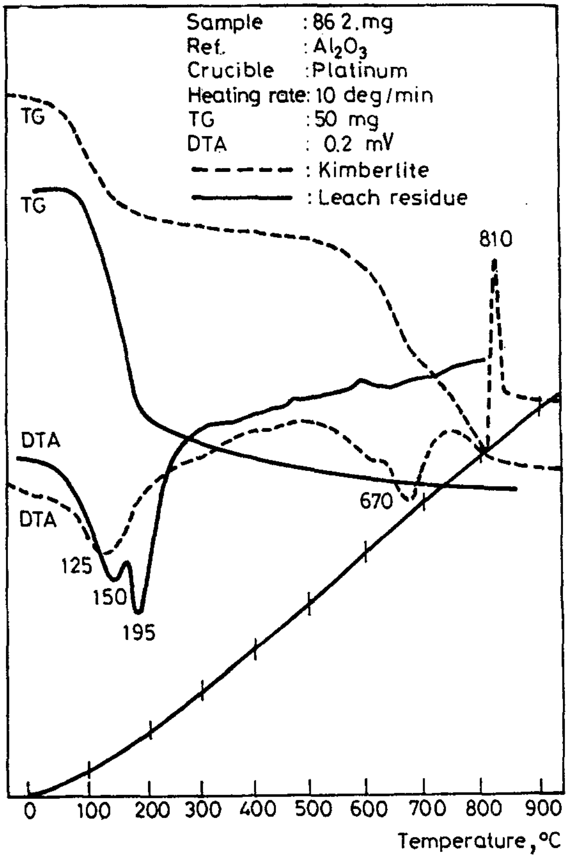

Fig. 3 DTA and TG curve of H_2SO_4 leach residue and Kimberlite tailings

100° for 5 hrs leaching time, in order to maintain a $pH \geq 3$, where most of the ferric iron and silica remain in the residue. The recovery of metal values are magnesium 85%, iron 25%, calcium 4% and silica 6.2%.

Leach residue analysis

Comparison of the XRD of the leach residue (Fig. 1) shows the disappearance of serpentine and magnetite phases and appearance of additional peaks corresponding to $CaSO_4 \cdot 2H_2O$ and free silica. The TG-DTA curve of the residue (Fig. 3) indicates the endothermic peaks at 150° and 190° corresponding to the dehydration of $CaSO_4 \cdot 2H_2O$ and also disappearance of endothermic peak at 670° (for the dehydroxylation of serpentine) due to leaching of magnesium from the serpentine phase.

Purification of leach liquor and crystallisation

The leach liquor containing impurities such as iron, calcium and silica was treated with 20% lime slurry [10] to adjust the *pH* to 5.5 followed by aeration for 2 hrs at 65°. Most of the iron (97%) was precipitated and the final *pH* of the slurry was 3.5. After filtration, the filtrate was again subjected to the removal of the remaining iron. Magnesium sulphate thus obtained was crystallised by evaporation with a yield of 75%.

Characterisation of product magnesium sulphate

The product $MgSO_4 \cdot 7H_2O$ was characterised by XRD, DTA and spectral analysis studies and compared with Analar grade (BDH) sample. The optical emission spectroscopic analysis of the product magnesium sul-

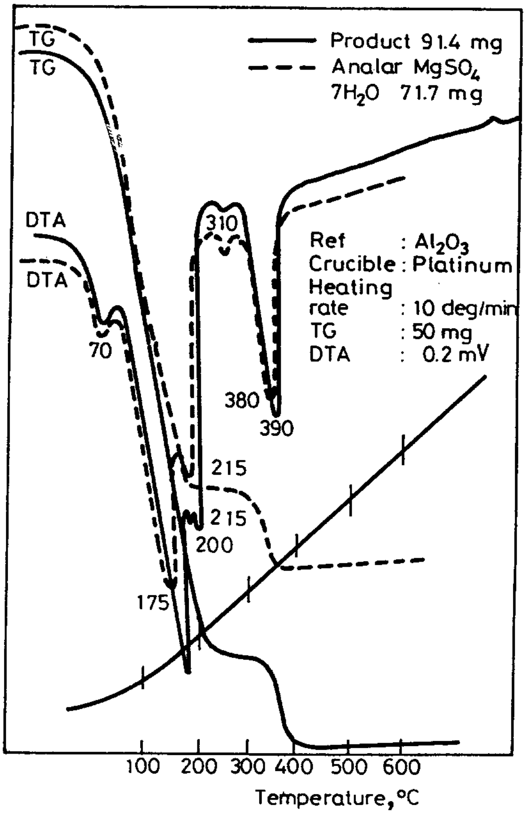

Fig. 4 DTA and TG curve of product from Kimberlite tailings and Analar $MgSO_4 \cdot 7H_2O$

Table 1 Optical emission spectroscopic analysis for BDH Analar grade and product $MgSO_4\cdot 7H_2O$ obtained from H_2SO_4 leach liquor

Element	Si	Al	Fe	Ca	Ti	Na	K	P	Mn	Cd	Pb
Product from Kimberlite	A	Tr	Tr	M	nd	nd	nd	Tr	M	nd	Tr
BDH Analar $MgSO_4\cdot 7H_2O$	Tr	nd	mtr	vf	nd	nd	nd	nd	A	nd	nd
Element	Cr	V	Zn	Ni	Mo	B	Cu	Co			
Product	nd	nd	Tr	Tr	nd	Tr	Tr	nd			
Analar	nd	nd	nd	nd	Tr	nd	nd	nd			

M, major; *A*, appreciable; *Tr*, Traces; *mtr*, minute traces; *vf*, very feeble; *nd*, not detected

Table 2 Comparison of % weight loss from the product obtained from Kimberlite and Analar $MgSO_4\cdot 7H_2O$ by TG (Fig. 4)

°C	Theoretical	Product	Analar $MgSO_4\cdot 7H_2O$ (99.5–103.0%)
40–220 ($-6H_2O$)	43.90	44.85	44.07
310–380 ($-H_2O$)	7.30	7.00	8.08
40–380 ($-7H_2O$)	51.22	52.51	52.16
Assay	100	102.7	101.9

Table 3 Comparison of major XRD peaks of product obtained from Kimberlite and Analar $MgSO_4\cdot 7H_2O$

ASTM		Product		BDH Analar	
d, Å	I/I_o	*d*, Å	I/I_o	*d*, Å	I/I_o
5.99	20	5.97	23	5.96	28
5.35	25	5.33	34	5.33	20
4.21	100	4.20	100	4.20	100
2.88	20	2.87	19	2.88	19
2.68	25	2.67	30	2.68	16

phate along with the Analar grade $MgSO_4\cdot 7H_2O$ is shown in Table 1 for comparison. The relative intensities for Ca, Fe, Al, Mn, Zn, Ni, Cu and B were found to be more with the product. The chemical analysis showed the presence of 0.05% Ca, 0.001% Fe, 0.002% Mn and other impurities only in the ppm level. The TG and DTA of both the product and BDH Analar sample are presented in Fig. 4. The patterns look alike and the percentage weight losses are similar corresponding to the dehydration of $MgSO_4 \cdot 7H_2O$ (Table 2). The major XRD peaks of the product and BDH Analar sample are compared in Table 3. From the above results, it is seen that both chemical and instrumental analysis confirm the purity of the product $MgSO_4 \cdot 7H_2O$ produced through the sulphuric acid leaching of weathered Kimberlite tailings in comparable limits with that of Analar grade sample.

Conclusions

Characterisation studies involving XRD, TG–DTA and spectral analysis would play a significant role at different stages during the development of flow sheet in chemical processing of Kimberlite tailings.

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Zusammenfassung — Mittels DTA und Röntgendiffraktion wurden verwitterte Kimberlit-Abgänge aus Diamantbergwerken in Panna charakterisiert. Das Röntgendiagramm zeigt die Gegenwart von Serpentin-, Quarz-, Kalzit-, Hämatit-, Magnetit- und Anatas-Phasen. Die DTA-Kurve zeigt einen ersten endothermen Peak bei 125°C (Dehydratation des Minerales) und einen zweiten endothermen Peak bei 670°C (Dehydroxylierung von Serpentin), eng gefolgt von einem exothermen Peak bei 810°C (Bildung von Forsterit). Röntgendiffraktions- und DTA-Untersuchungen an einem schwefelsauren Extraktionsauszug von Kimberlit zeigen das Verschwinden der Serpentin-Phase, aber das zusätzliche Auftreten einer $CaSO_4 \cdot 2H_2O$-Phase. Nach Reinigung und Kristallisation wurde $MgSO_4 \cdot 7H_2O$ als Produkt erhalten, dessen optische emissionsspektroskopische Untersuchung in Spuren Verunreinigungen mit Ca, Fe und SiO_2 zeigten.