Thermal analysis of inorganic materials

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1. Introduction

Thermogravimetry (TG) studies the change (gain or loss) of a sample mass as a function of temperature and/or time. The measurements of these changes are made using a thermobalance in which the tests are accomplished according to a programed heating rate in a suitable enclosed system with a controlled atmosphere.

The application of thermogravimetry to inorganic gravimetric analysis caused a real revolution in the early 1950s. Today, thermogravimetry resolves many analytical problems in inorganic chemistry, ceramics, metallurgy, pigment development, mineralogy and geochemistry. Application of thermogravimetry is limited to events with detectable mass changes Otherwise, other techniques, such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC), must be used. The main inorganic thermal events recorded by TG are summarized in table 1

Table 1. Main thermal events registered by TG in inorganic materials

Sublimation	A (solid) → A (gas)
Vaporization	A (liquid) → A (gas)
Adsorption	A (solid) + B (gas) → A (solid) ($B_{gas\text{-}ads}$)
Absorption	A (solid) + B (gas) → A (solid) ($B_{gas\text{-}abs}$)
Desorption	A (solid) ($B_{gas\text{-}ads}$) → A (solid) + B (gas) A (solid) ($B_{gas\text{-}abs}$) → A (solid) + B (gas)
Oxidation	A (solid) + B (gas) → C (solid)
Pyrolisis	A (solid) → B (solid) + Gases
Volatilization	A (solid) + B (gas) → Gases
Heterogeneous catalysis	A (solid) + $(\text{Gases})_1$ → A (solid) + $(\text{Gases})_2$

There is an absorption (endothermic process) or a emission (exothermic process) of heat when a material has a change of physical state or chemical reaction. Differential thermal analysis (DTA) measures the difference of temperature between a sample and a reference (ΔT) versus temperature, whereas, differential scanning calorimetry (DSC) records the differences of heat quantity between a sample and a reference versus temperature. In both techniques a programmed heating rate is applied. DSC gives a value for the amount of absorbed or evolved energy in a particular transition and, therefore, also provides a direct calorimetric measurement.

Applications of DTA and DSC to inorganic samples are:

- Determination of enthalpy in phase changes
- Determination of phase diagrams
- Determination of enthalpy in chemical reaction
- Kinetic analysis
- Identification and characterization

2. Quantitative chemical analyisis

2.1. Determination of alkaline-earth elements in dissolution

The quantitative analysis of Ca^{2+}, Sr^{2+} and Ba^{2+} in aqueous solution is possible by TGA (1). The separation of these ions is carried out with ammonium oxalate to give mixed metal oxalate hydrates which are decomposed on the thermobalance (figure 1). The following steps are observed in the TG and DTG plots:

- Loss of hydratation water (step A)
- Decomposition of the three anhydrous metal oxalates to metal carbonates and CO (step B):
  - $CaC_2O_2 \rightarrow CaCO_3 + CO$
  - $SrC_2O_2 \rightarrow SrCO_3 + CO$
  - $BaC_2O_2 \rightarrow BaCO_3 + CO$
- Calcium carbonate decomposition $CaCO_3 \rightarrow CaO + CO_2$ (step C)
- Strontium carbonate decomposition $SrCO_3 \rightarrow SrO + CO_2$ (step D)
- Barium carbonate decomposition $BaCO_3 \rightarrow BaO + CO_2$ (step E)

The amounts of calcium, strontium and barium can be calculated according to the following equations:

$$Ca = \frac{Atomic\ \ mass\ \ (Ca)}{Molecular\ \ mass\ \ (CO_2)}.\ Mass\ \ loss\ (C)$$

$$Sr = \frac{Atomic\ \ mass\ \ (Sr)}{Molecular\ \ mass\ \ (CO_2)}.\ Mass\ \ loss\ \ (D)$$

$$Ba = \frac{Atomic\ \ mass\ (Ba)}{Molecular\ \ mass\ (CO_2)}.\ Mass\ \ loss\ (M)$$

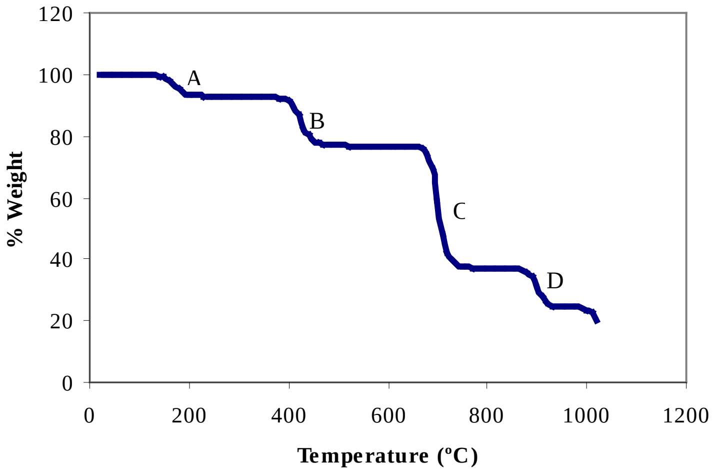

Figure 1. TGA curves of calcium, strontium and barium oxalates hydrates

2.2. Calcium and magnesium analysis in dolomite

Dolomite is a double carbonate of magnesium and calcium containing 30.41% of calcium oxide (CaO), 21.86% of magnesium oxide (MgO) and 4.73% of carbon dioxide (CO_2). As an ore, it facilitates the process of obtaining magnesium. It is used as a building and ornamentation material, and in the manufacture of certain elements. As a raw material it is employed to obtain magnesia [$(OH)_2Mg$], itself used in iron and steel refractory coatings, and as flux material in the metallurgical industry. Figure 2 shows the TG plot for dolomite. There is loss of water up to 200ºC. Magnesium carbonate decomposition appears at 470ºC ($MgCO_3$)

$$MgCO_3 \rightarrow MgO + CO_2$$

DE corresponds to a mixture of MgO and $CaCO_3$

Between 600 and 850ºC is the calcium carbonate decomposition

$$CaCO_3 \rightarrow CaO + CO_2$$

FG corresponds to a mixture of MgO and CaO

The difference, W_1-W_2 is equal to the mass of carbon dioxide that develops between 500 and 900ºC by the decomposition of calcium carbonate. The amount of calcium oxide is given by:

$$W(CaO) = (W_1-W_2).56/44 = (W_1-W_2)\cdot 1.272$$

Where 56 is the CaO molecular weight and 44 the CO_2 molecular weight, and the difference (W_1-W_2) is the CO_2 mass evolved between 500 and 900ºC.

The amount of magnesium oxide is given by the difference

$$W(MgO) = W_2 - W (CaO)$$

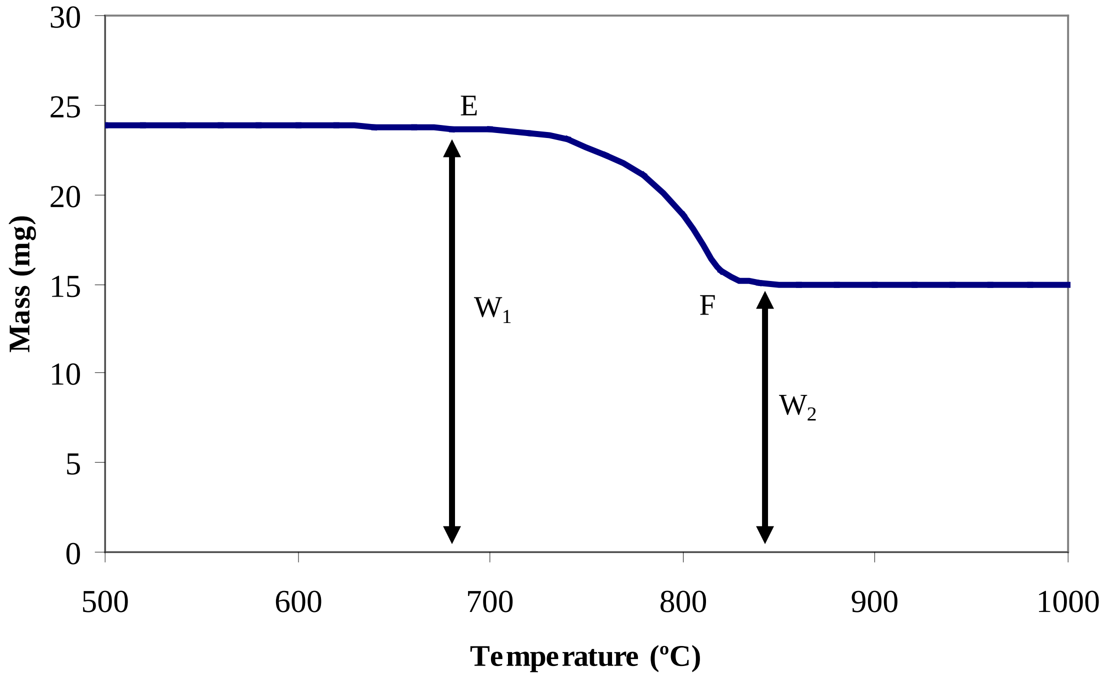

Figure 2. TGA curve of dolomite

3. Clays

3.1. Kaolinite

Kaolinite´s formula is $Al_2Si_2O_5(OH)_4$. Humans have been using this material in different ways from time immemorial. In the fifteen century, porcelain made of ceramics with a high content of kaolin acquired great fame among the nobility. Nowadays, the main consumer of kaolin is the paper industry, which uses more than 50% of the production as filler, and to give a superficial finish, or stucco, to paper. Also, the manufacturing of ceramic materials (porcelain, stoneware, crockery, sanitary pottery and electroceramics) and refractory (thermal insulators and cements) are important. Kaolinite is found as a secondary mineral formed by the weathering or hydrothermal alteration of aluminum silicates, particulary feldspars. It occurs naturally in almost every country of the world.

Figure 3 shows the TG curve of kaolinite. Absorbed water is gradually evolved at temperatures up to 200ºC (in this case the mass-loss is 0.8% of the sample). The dehydroxylation reaction occurs in the temperature range of 400-700ºC giving a mass-loss of 13.4%. Experimental factors, such as the heating rate, large sample particle size and so on can shift the initial and final temperatures of the dehydroxylation.

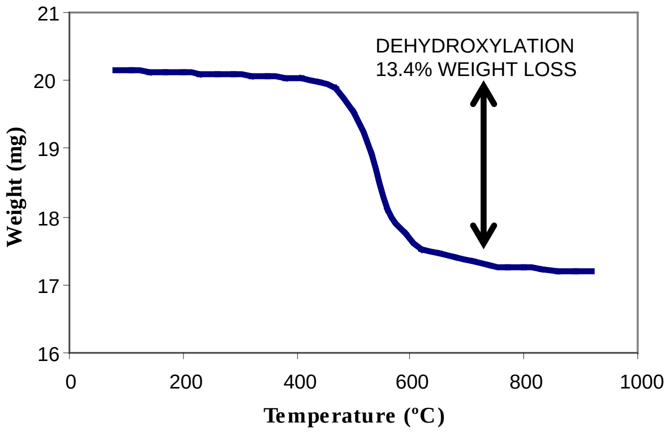

Figure 3. TGA curve of kaolinite

A typical DSC plot of kaolinite is shown in Figure 4. The following peaks can be observed in it:

- Desoprtion of water from ambient to 110ºC (Endotherm); seldom observed by DTA and DSC except in highly disordered species. Easily observed by TG and DTG.
- Dehydroxilation of crystal lattice (450-700ºC) (Endotherm process with a Tmin=540ºC). The main endothermic peak. Observed in all members of the group except allophane.
- Spinel-type structure cristalization (900-1000ºC) (Exotherm process with a Tmax=990ºC).
- Formation of mullite (1100ºC up) (Exotherm process).

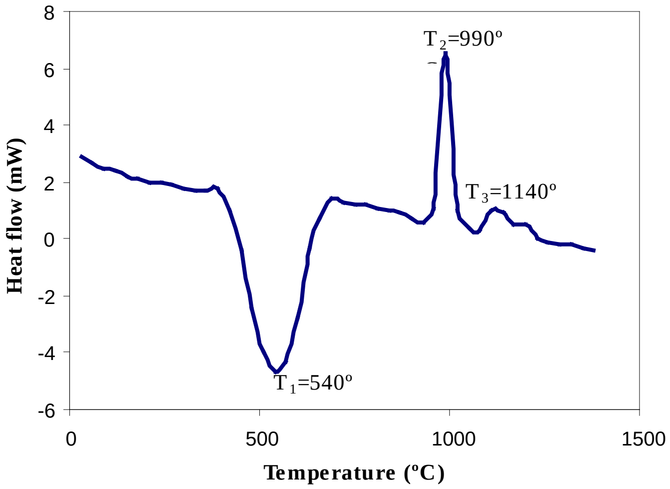

Figure 4. DSC curve of kaolinite

3.2. Hectorite

Hectorite [$Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$] is a clay mineral, with a similar structure to that of bentonite. It belongs to the smectites group. It has a soft greasy texture and feels like modeling clay when squeezed between the fingers. It is one of the more expensive clays, due to its unique thixotropic properties. The main uses of hectorite are cosmetics (lotions, soaps, creams and shampoos), coatings and inks. It is also employed as molding sand in metal casting and as filler in the paper industry. It has a great capacity to absorb and to adsorb because of its high specific surface. It plays an important part in industrial water purification and the discoloration of oil, wine, cider and beer.

Hectorite geological samples are usually associated with large amounts of calcite, in some cases with varying amounts of dolomite. Thus, most published thermal analysis curves reflect the thermal behavior not only of hectorite but also of carbonates. Figure 5 shows a typical DTA curve of hectorite. At an endothermic peak at ΔT_{min} of 119ºC is caused by the interlayer water loss, whereas the 742 and 838ºC peaks are due to the dehydroxylation/carbonate decomposition reactions. A narrow exothermic peak at 1110ºC is followed by endothermic peaks at 1135 and 1255ºC. The latter are probably due to the formation of clinoenstatite.

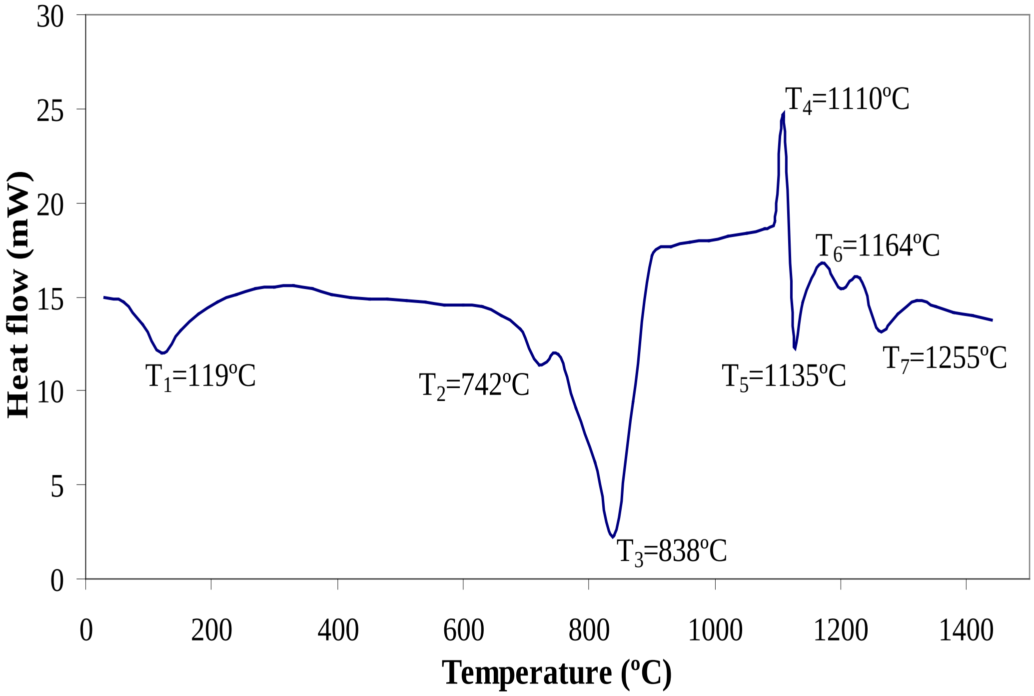

Figure 5. DSC curve of hectorite

4. Concrete and mortars

Concrete is a mixture of cement clinker, water, gypsum ($CaSO_4.2H_2O$), and aggregates such as quartz, limestone, dolomite, and slag. Clinker is produced by the reaction of calcium oxide (CaO=C), silica (SiO_2=S), alumina (Al_2O_3=A) and ferric oxide (Fe_2O_3=F) at about 1500ºC to give tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and ferrite solid solution of composition between C_2F and C_6A_2F often represented as C_4AF. The hydratation and hardening of Portland cement takes place as a result of the following reactions:

$$2\ C_3S + 6\ H_2O \rightarrow C_3S_2.3H_2O + 3\ Ca(OH)_2$$
$$2\ C_2S + 4\ H_2O \rightarrow C_3S_2.3H_2O + Ca(OH)_2.$$

The tricalcium silicate trihydrated derived from this reaction has extremely small particles and it forms a colloidal suspension. Calcium hydroxide (portlandite) is a crystalline solid. The hydration products of other cement components are not generally described as producing portlandite.

If thermogravimetric analyisis is carried out in carbon dioxide at atmospheric pressure, the first event will be dexhydroxylation at 400ºC of any portlandite present in recently made concrete

$$Ca(OH)_2\ (s) \rightarrow CaO\ (s) + H_2O\ (g)$$

But the amount of $Ca(OH)_2$ is very small amount old concrete because of the reaction of portlandite with carbon dioxide over many years:

$$Ca(OH)_2\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2O\ (l)$$

Dollimore et al. (2) showed the importance of this last reaction in the thermal analysis of dolomite used in recycled portland cement concrete (RPCC) as an aggregate. Dolomite in N_2 decomposes in a single step:

$$CaMg(CO_3)_2\ (s) \rightarrow CaO\ (s) + MgO\ (s) + 2\ CO_2\ (g)$$

but in the presence of CO_2, figure 6, ithe dolomite dissociation is divided into two steps:

$$CaMg(CO_3)_2\ (s) \rightarrow MgO\ (s) + CaCO_3\ (s) + CO_2\ (g) \text{ at } 780^{\circ}C$$
$$CaCO_3 \rightarrow CaO\ (s) + CO_2\ (g) \text{ at } 910^{\circ}C$$

The first dissociation permits the dolomite weight percentage to be calculated. In the second step, part of the $CaCO_3$ comes from portlandite carbonation.

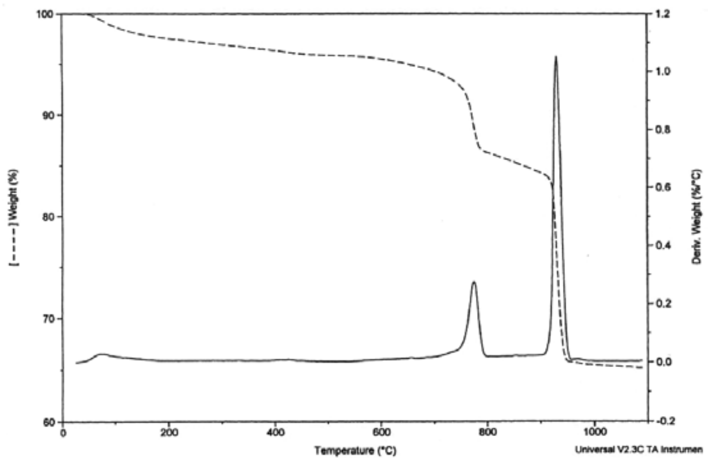

Figure 6. TG and DTG for recycled cement concrete (RPCC) carried out in a flowing atmosphere of CO_2 (100 ml/min) at a heating rate of 10ºC/min (2) (With permission of Elsevier).

On the other hand, the DTA curves of ancient concretes show the existence of an endothermic peak at 570ºC (figure 7). This peak is related to the allotropic transformation of quartz (3):

$$\alpha\text{-}SiO_2 \rightarrow \beta\text{-}SiO_2$$

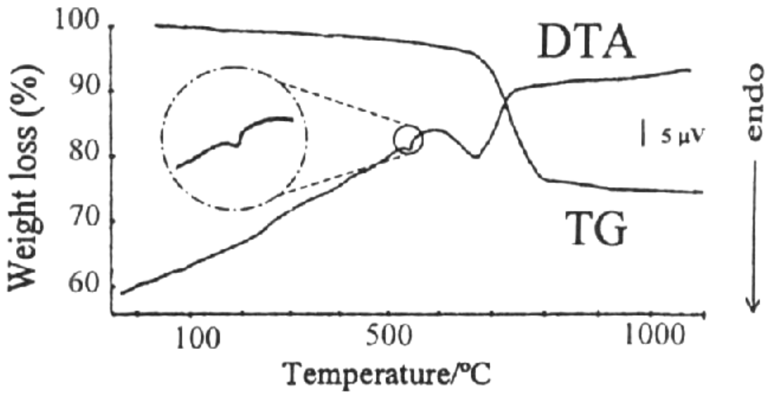

Figure 7. DTA and TG curves from a Pamplona cathedral mortar (3) (With permission of Elsevier).

Another component of concrete and mortars is gypsum. Natural gypsum formula is $CaSO_4.2H_2O$). If two molecules of water are removed, anhydrite ($CaSO_4$) is produced. There are two anhydrite forms, one which hydrates with water (soluble anhydrite), and the other which shows no tendency to react with water (insoluble anhydrite). Figure 8 shows the differential thermal analysis of a $CaSO_4.2H_2O$ sample heated at 20ºC/min (4). Crystallization water was partially removed starting from 123ºC to produce the hemihydrate form ($CaSO_4 \cdot 0.5H_2O$) also called bassanite or plaster of Paris. The second peak at 202ºC is due to the loss of $0.5H_2O$ to form soluble anhydrite ($CaSO_4$). The exothermic peak between 353 and 375ºC represents the phase change to insoluble anhydrite

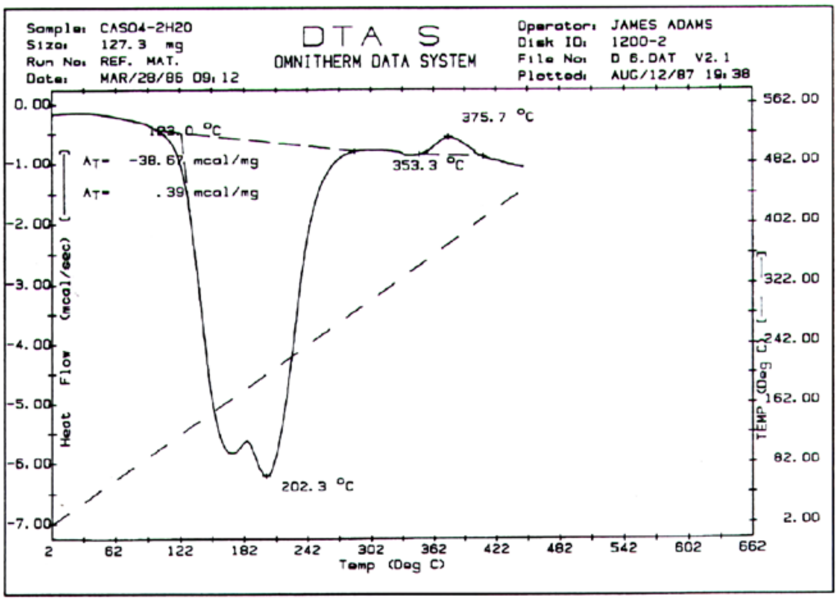

Figure 8. DTA of calcium sulfate dihydrate (4) (With permission of Elsevier)

5. Pigments

5.1. Egyptian blue

Egyptian blue, $CaCu(Si_4O_{10})$, is a very stable pigment which can be found in many works of art from the Egyptian, Mesopotamian, and Roman civilizations. This compound can be synthesized in a thermobalance heating a mixture of quartz (SiO_2), cupric oxide (CuO), calcite ($CaCO_3$), and a fluxing agent (Na_2CO_3, borax or PbO). Without these fluxing agents, the reaction proceeds very slowly, leading to an impure product which does not have the intense blue colour of the pigment. With borax, for instance, the reaction mixture forms $CaCu(Si_4O_{10})$ at about 900ºC at a heating rate of 4ºC/min and remains stable in an oxidizing atmosphere to about 1080ºC. Above this temperature, it decomposes to give off trydimite and a mixture of CuO and Cu_2O due to the reduction of Cu^{2+} to Cu^{+} (figure 9). However the initial compound does not form again on cooling even though Cu^{+} deoxidizes to Cu^{2+} (5-6).

The thermal stability of the isoestructural compounds $SrCu(Si_4O_{10})$ and $BaCu(Si_4O_{10})$ is greater then in the calcium compound, since they decompose at 1155 and 1170º respectively. Single crystals of the Ca, Sr, Ba compounds can be grown by using borax, PbO, or Na_2CO_3 flux with heating cycles of 30 hours at about 900ºC. These crystals are similar to some Egyptian blue samples obtained from archaeological excavations.

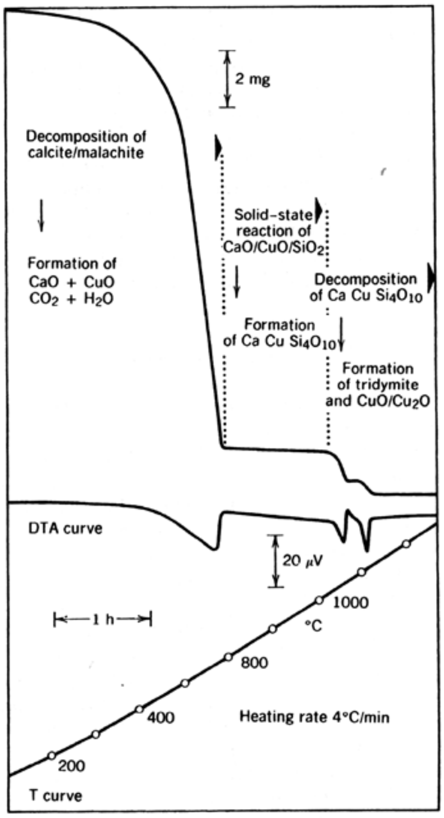

Figure 9. TG-DTA-T curves showing the formation of Egyptian blue from calcite-CuO-quartz mixture (5) (With permission of American Chemical Society)

6. Extractive metallurgy

6.1. Thermal behavior of $AlF_3.H_2O$

Aluminum fluoride is used as flux in the electrolytic reduction of alumina (Al_2O_3) to produce metal aluminium. In the wet process, the anhydrous fluoride is prepared by heating trihydrated aluminum fluoride. This thermal decomposition involves three stages:

$AlF_3.3H_2O \rightarrow AlF_3.0,5H_2O + 2,5\ H_2O$ de 108 a 277°C
$AlF_3.0,5H_2O \rightarrow AlF_3 + 0,5H_2O$ de 277 a 550°C
$AlF_3 + 3\ H_2O \rightarrow Al_2O_3 + 6\ HF$ >380°C

Figure 10 shows Tg and DTG curves for $AlF_3.3H_2O$ and the system $AlF_3.3H_2O/MgO$ at a heating rate of 10°C/min (7).The first stage, with the temperature in the range from 100 to 277ºC and a mass loss of 32.7% is related to the loss of 2.5 molecules of water from $AlF_3.3H_2O$. The value of mass loss in the second stage (6.9%) corresponds to the formation of anhydrous aluminum fluoride. As temperature exceeds 380ºC, aluminum fluoride reacts with water to give alumina (Al_2O_3).

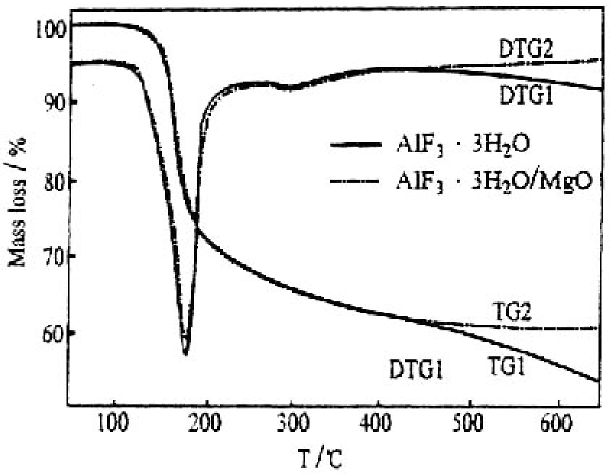

Figure 10. TG-DTG curves of AlF_3-$3H_2O$ and system $AlF_3.3H_2O//MgO$ at heating rate of 110ºC/min (7) (With permission of Elsevier)

6.2. Thermal oxidation of covellite

Covellite usually exists in small quantities associated with other sulphides as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). Heating covellite in an oxidant atmosphere causes the formation of copper deficient compounds at low temperatures and the oxidation to sulphates and oxides at higher temperatures.

Dunn and Muzenda (8) carried out TGA/DTA tests with covellite samples at 20ºC/min in dry air (figure 11). They analyzed the evolved gases by use of coupled FTIR equipment. The first stage is the decomposition of a small amount of covellite to give digenite ($Cu_{1,8}S$) and the oxidation of covellite to produce copper (I) sulphide. These reactions give an exothermic peak in the DTA curve and a mass-loss in TGA curve between 330 and 422ºC

$$1{,}8\ CuS + 0{,}8\ O_2 \rightarrow Cu_{1,8}S + 0{,}8\ SO_2$$
$$2\ CuS + O_2 \rightarrow Cu_2S + SO_2$$

Between 422 and 474ºC there is a mass gain associated with an exothermic peak due to Cu_2S oxidation to Cu_2SO_4 according to the global reaction:

$$Cu_2S + 4\ O_2 \rightarrow 2\ CuSO_4$$

Another exothermic peak and associated mass gain appears in the temperature 474-585ºC. This event was related to a solid-solid reaction between Cu_2S and $CuSO_4$ to form Cu_2O (exothermic peak) and sulfation of the oxide formed (mass gain).

$$Cu_2S + 2\ CuSO_4 \rightarrow 2\ Cu_2O + 3\ SO_2$$
$$Cu_2O + 2\ SO_2 + 1.5\ O_2 \rightarrow 2\ CuSO_4$$

Also, the presence of $CuO.CuSO_4$ was detected in the melt at 583ºC probably due to this proposed reactions:

$$2\ CuSO_4 \rightarrow CuO.CuSO_4 + SO_2 + 0.5\ O_2$$
$$Cu_2O + 4\ CuSO_4 \rightarrow 3\ CuO.CuSO_4 + SO_2$$

The formation of $CuO.CuSO_4$ continued up to 653ºC, at which an endothermic peak and a mass-loss started. This last stage was related to the decomposition of $CuO.CuSO_4$ to CuO.

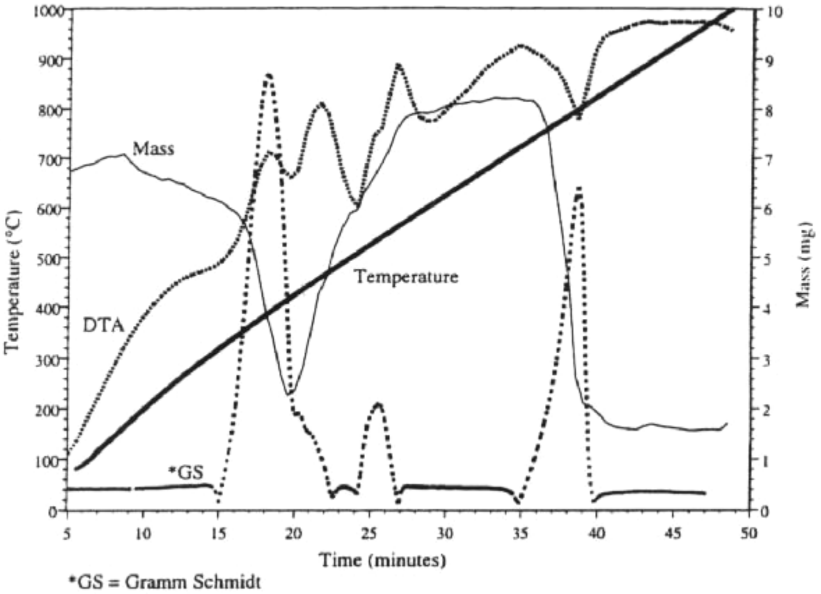

Figure 11. TGA-DTA-FTIR records for the oxidation of covellite from ambient to 820ºC in dry air at heating rate of 20ºC/min (8) (With permission of Elsevier).

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