APPLICABILITY OF THE INFRARED SPECTROSCOPY IN THE EXAMINATION OF REFRACTORY MATERIALS

I. GYÖRGY*, É. BIHARI and A. CSER

Magnesite Industry Budapest

Summary

A desintegrated magnesite-chrome brick of a cement-burning rotary kiln has been examined by IR spectroscopy. The IR method has proved to be suitable to the identification of the infiltrated brick portions and sediments. We have found that the deterioration of the bricks is attributable to the fact, that the silicate clinker-phases react with the magnesia-sinter.

On the basis of the IR research results we have changed the production technology of magnesite-chrome bricks.

Introduction

The refractory building materials are the indispensable ingredients of the steel, cement and glass-industry. The following three main groups are used:

— Silica-products (silica-chromesilica, zirconsilica), quartz-glass products
— Aluminiumsilicate products (corund, mullite, chamotte)
— Basic, not silicate products, as magnesite, dolomite, chrome-magnesite, magnesite-chrome, chromite, forsterite.

In the silicate industry the basic refractories are mostly in use. To meet the always higher and higher demands concerning the new products, it was intended to detect, how the infrared spectroscopy among other methods can be used in the examination of the refractories. On the other hand, it was of interest, how the method can answer the questions of changes, occurring upon their use in the furnaces. Especially how the method can be useful in the detection of corrosion taken place in the furnaces, what answer it is able to give in this respect.

The infrared investigation of refractories

The users of these materials have realized that the physical investigation values of the refractories alone are not characteristic.

The knowledge of the original and end-product is necessary to the development of new products.

* Central Research and Design Institute for Silicate Industry, H 1032 Budapest Bécsi út 120

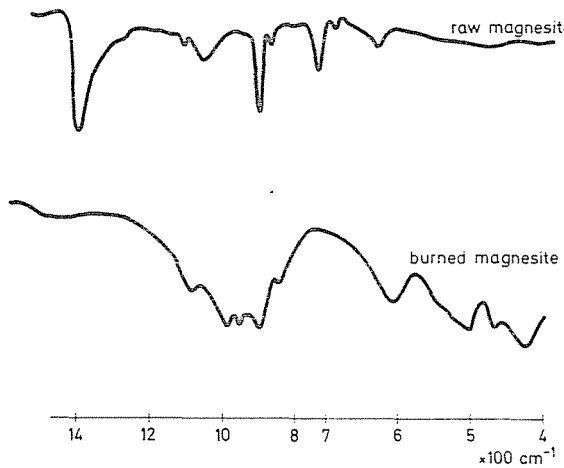

Fig. 1. Infrared spectra of raw and burned magnesites

The infrared spectroscopy in this respect is very useful by the investigation of the raw-materials, of their qualitative and quantitative testing. As an example in Fig. 1 one can see a raw-magnesite impurity contamination by dolomite and magnesium-silicate and the infrared picture of a sintermagnesite.

The raw-magnesite with the characteristic absorption band of his carbonate groups

$$\nu_3 \text{ (asymmetric stretching) by } 1450\ \text{cm}^{-1}$$

$$\nu_2\,,\ \nu_4 \text{ (bending vibration) at } 895\ \text{cm}^{-1} \text{ and } 775\ \text{cm}^{-1}$$

is distinguishable from all other carbonate minerals (calcit–dolomit–aragonit group). These different absorption bands find their explanation in the infiltration of the different mass-quantity of the cations and their measure (ion-radius).

The qualitative identification can be carried out in this way.

The infiltrated minerals so exists a possibility of the determination of the quantity of magnesite-dolomite proportion.

In case of a complex constructional investigation the IR method can be used as part of the supplementary method of the X-ray declination method.

In the last two decades in the cement industry the rotary kiln burning has been ruling.

In the sinter-zones of the rotary kilns invariably the basic bricks are used, what is motivated by the highly extended application of the kilns. As a consequence of the enlarged load the infiltration becomes higher, the local

overheating, the thermic endurance and the smaller protective layer formation cause erosive influence.

On this basis the wearing out of the lining is attributed to the following three main reasons:

1) Material exchange processes causing structural changes alter the strength of the bricks
2) Strains causing the breaking of the bricks: broken pieces fall out of the lining
3) Erosion occurring upon the wear-action of the clinker and showing abrasive signs of the fire-side.

Concerning the basic bricks for the cement industry in the sinter-zone the magnesite-bricks with chrome-additives proved to be the best. In the traditionally made magnesite-chrome brick the macro-structure is characterized by the chrome ore grain which is embedded in a heterogeneous magnesite matrix. This grain, though it ensures the good bearing of thermal differences, deteriorates the structure of the brick. Fusions are intrusing into the micro-cracks, like capillaries and on the influence of the heat-gradients they solidify according to their melting points.

The elastic microstructure ceases to exist on the influence of the spalling. The infiltrated part comes down in form of a flaw from the brick in approx. 20–30 mm layers.

We were looking for a suitable method to identify the chemical changes occurring in the brick.

It is known from literature, that with X-ray diffraction method the infiltrated melts in the capillaries cannot be seen, because their concentration is smaller than the detection limit. The IR spectroscopy has proved to be suitable to the identification of the infiltrated brick portions and sediments.

The IR-spectroscopy of the magnesite-chrome bricks used in the cement burning rotary kilns

A desintegrated magnesite-chrome brick of a cement-burning rotary kiln has been examined on its fire-side and inside. We also examined the outer side, which has shown a yellow melt.

Out of all zones the same quantity powdered under a size of 10 micron was taken and many spectra recorded with the KBr pellet-making system using the UR-10 device. Figure 2 shows a characteristic IR-spectrum from the fire-side of the brick (a) and from its middle (b), i.e. from its expressed yellow discoloured melt. In all three spectra the presence of sulphate was clearly proved by 1120 cm^{-1} and 620 cm^{-1} wave numbers.

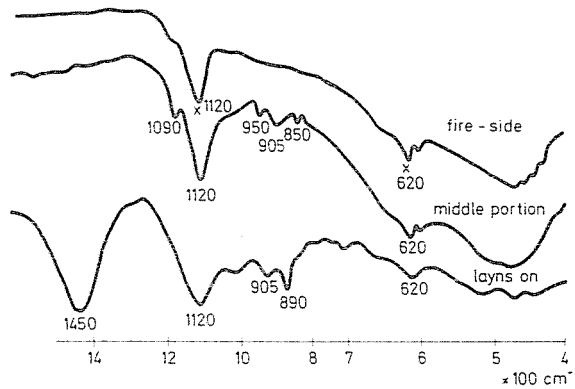

Fig. 2. Infrared spectra of the characteristics of the deteriorated bricks

This probably comes from the sulphur content of the fuel and being discoverable also in the middle of the brick, it infiltrates deep into the brick and constitutes calciumsilicate mixed crystals. This is proved by the IR-data of the pure and mixed crystals developing out of the former [1].

At the same time on the yellowish scalding spurrit (1450 cm^{-1}, 950 cm^{-1}, 905 cm^{-1}) i.e. CrO_4^{2-} (890 cm^{-1}) is demonstrable. Out of the above mentioned follows that the deterioration of the bricks can be attributed to the fact that the silicate clinker-phases react with the magnesia-sinter. The process is urged by the presence of alkali-sulfates.

This explanation is supported also by literature references.

On the basis of the IR research results the production technology of magnesite-chrome-bricks was changed so, that the magnesite grains be embedded into a matrix of magnesia-spinels solid solution.

By this measure the micro-flaws became smaller and the solution of magnesia-spinells woven through and through with pores becomes less wet.

The formation of spurrit compound falls back or even ceases to exist of all.

Reference

1. TROJER, F.–OBST, K. H.–MÜNCHBERG, M.: Applied Mineralogy, Springer Verlag, Wien, 1981.

Ilona GYÖRGY — Central Research and Design Institute for Silicate Industry, H-1032 Budapest Bécsi út 120

Éva BIHARI, Arisztid CSER — Magnesite Industry, H-1103 Budapest Gyömrői út 48