PYROLUSITE (MnO_2) FROM IMINI: USE AND NEW APPLICATIONS IN CERAMICS

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INTRODUCTION

The progressive shortening of firing cycles requires ever stricter control of black core treatment. In this sense, the studies performed on micronized dioxide from IMINI (SACEM) in the form of concentrated pyrolusite, confirms an economically feasible option for the ceramic industry.

A summary is given of the laboratory studies as well as some semi-industrial or industrial experiments carried out over the last two years in fine ceramics as well as in structural ceramics, using concentrated pyrolusite from a mine in IMINI (Morocco).

In the second part of the study, mainly based on experiences in Spain, the technical-economic aspects of pyrolusite applications are dealt with, relative to the current situation and middle-term prospects, as are the side effects arising from the use of micronized pyrolusite in the process of reducing black core in fine ceramics.

I.- SUMMARY OF LABORATORY TESTS AND SEMI-INDUSTRIAL OR INDUSTRIAL TRIALS USING PYROLUSITE

1) MINERALS

Manganese is present in about 300 natural minerals; however in most of these, it is found in small proportions.

Minerals may be classified in various groups, the most common being:

a.- Pure manganese dioxides: α MnO_2 or cryptomelane; β MnO_2 or pyrolusite; γ MnO_2 or nstutite; δ MnO_2 or birnesite

b.-Combinations with other elements:
Psilomelane (combination with barium)
Braumite, rhodonite, tephroite (combination with SiO_2)
Bementite, bixbyite, jacobsite (combination with iron)

In the ceramic industry, the presence of pyrolusite (mainly found in Moroccan minerals) will yield a much greater reactivity for developing a grey/brown/black colour in red clays, or provide oxygen at certain temperature rates.

Particle size must therefore be taken into account as well as the final type of manganese dioxide, the type of clay used and the firing conditions applied for obtaining the mix that will enable the most suitable product to be determined in the best economic conditions.

2) SELECTION OF THE GRADES USED:

The studied manganese dioxides came from a Moroccan mine in IMINI, which has the only mineral known to date with such a high pyrolusite content.

The following elements were found among the other phases:
Psilomelane: 4 MnO_2 (Mn, Ba, Ca, O)$_2$; dolomite: Ca Mg CO_3; apatite: Ca_3 $(PO_4)_2$;
Rhodonite: $MnSiO_3$. Pyrolusite has a needle-like shape whereas psilomelane is granular.

The mining process is based on selecting the fines by air separation, which allows recovering a large percentage of pyrolusite and having a range of natural products or 70-92% MnO_2. The presence of needles of pure β MnO_2 encourages reactions with the clays.

The mine yields various particle size fractions:
UF Quality 0-75 μm. UFM Quality 0-30 μm. UM Quality 0-10 μm
In the ceramic industry, the grades UF 74 to UF 80 and UFM 80 represent the best choices from a technical-economic viewpoint.

Summing up, it became clear as a result of the tests and trials run on reducing black core, that the richer the MnO_2 (70-92% for the IMINI product), and the higher the pyrolusite concentration and the more micronized it is (both parameters are closely linked in the specific IMINI process, which goes from ultra fine UF 0-75 microns to ultra micronized UM 0-10 microns, via the intermediate ultra fine micronized UFM of 0-30 microns), the more reactive are the resulting products. For economic reasons, intermediate grade UFM 80 was chosen for use in black core treatment.

3) THERMOGRAVIMETRIC ANALYSIS:

The theoretical study of phase transformations is based on formation enthalpies of the products. Knowing these latter values allows determining the transformation temperatures and necessary energies for a set oxygen pressure.

The reactions for MnO_2 are as follows:
$2\ MnO_2 \rightarrow Mn_2O_3 + 1/2\ O_2$ theoretical temperature 530°C
$3\ Mn_2O_3 \rightarrow 2\ Mn_3O_4 + 1/2\ O_2$ theoretical temperature 1088°C
The first weight loss compared to starting weight is 9.2% and the second 3.1%. The theoretical study was confirmed by DTA of a MnO_2 UM of 74%. (Annex 2)

A third peak appears at 790°C owing to the presence of dolomite in the product.

a.- Influence of MnO_2 particle size: (Annexes 1 and 2)

Product reactivity corresponds to the surface of the endothermic point measured by DTA.

A finer product fraction will allow the proportion of pyrolusite to be raised and enhance its reactivity. Certain trials show this in the colouring, for instance mixing a UFM 80 with clay yields a brown with a lower low addition proportion than a UF 80.

The DTA curves do not allow this phenomenon to be identified, but the endothermic point due to dolomite disappeared at 800ºC (Annex 1).

b.- Influence of the MnO_2 percentage:

Annex 2 shows that the rise in MnO_2 content raises its reactivity and it has already been indicated that with regard to colouring, about 30% less is required than of the UF 80.

c.- Disappearance of the second endothermic point:

Often considered as a disadvantage in a temperature schedule where the glaze starts melting, the second endothermic point can be lowered by additives if need be (Annex 3).

4) EFFECT OF USING MnO_2 IN TREATING BLACK CORING

The presence of organic matter considerably reduces the possibilities of fast firing certain clays.

Different solutions are proposed:

- Raising the grog percentage, or excess air in the kiln, which would allow improving oxygen diffusion from outside inwards in the material to be fired.

- Another solution involves directly supplying oxygen by means of a raw material contained in the composition. Manganese oxide yields this oxygen at the ideal temperature schedule.

a.-Influence of the type of manganese used:

Using a well-known clay (red clay with 7% Fe_2O_3 and 1% organic matter), different tests were run with various types of MnO_2, using a linear firing cycle of 40ºC/min (with 30 min at 1200ºC).

The peak addition of 4% MnO_2 fully eliminated the black core in the clay (Annex 4). According to the purity or fineness of MnO_2, the addition can drop to 2% in this case, whereas in clays with less organic matter such as red and white Spanish clays, the proportion of grade UFM 80 needed ranged from 0.5 to 2% to eliminate black core.

b.-Influence of the firing cycle:

In fine ceramics with roller kilns (30 min cycles), the MnO_2 contribution must be associated with an optimized firing cycle. Generally, firing time must be reduced until the first black coring appears. The contribution of MnO_2 suppresses these phenomena and allows optimizing the firing cycle without changing the starting composition of the body to be fired.

In structural ceramics, involving kilns that have been adapted for 10-20 hour firing cycles, with materials containing a considerable percentage of organic matter, a horizontal firing segment must be determined (Annex 5).

c.- MnO_2 side effects:

- Meltability

Manganese dioxide fuses very efficiently and lowers porosity in the product. Studies are currently being undertaken to confirm how a given type of manganese affects final porosity.

• Colouring

- In slow cycles, manganese dioxide has well-known brown-colouring effects in red clays.
- In fast cycles, the colouring is less strong.
- In semi-fast cycles, of up to 5 hours from cold to cold, no colouring arises in roofing tiles and floor tiles for exterior applications, using calcareous clays with a percentage of MnO_2 (UFM 80), which does not exceed 0.7%, although it allows resolving the problem of black core.
- Floor and wall tile manufactured with white clays exhibit no significant changes in colour up to 1% de MnO_2.

II.- TECHNICAL-ECONOMIC ASPECTS OF USING PYROLUSITE

On the basis of experiences principally in Spain, conclusions may be drawn, albeit provisionally, from the work that has been carried out over the last two years, which although confirming the elimination of black coring, also indicate that there are certain side effects, and an economic balance to be drawn.

1) RANGE OF USES FOR MICRONIZED PYROLUSITE

a) The current situation may be defined in terms of the following parameters:

- What type of firing are we referring to? Fast firing is clearly involved, in cycles of less than an hour, and in many cases in fine ceramics of 40 min, using roller kilns, that is, in the greater part of production. Tunnel kilns with long firing cycles allowed problem-free outgassing, and black core reabsorption even with clays that were highly contaminated with organic matter.

In structural ceramics, to our knowledge, firing still takes place in slow cycles lasting over a day in Spain, but experiences in other European countries with semi-fast cycles of 10 hours for roofing tiles, suggest that different practices will arise in 4-5 years' time, when most companies will be upgrading their manufacturing facilities.

- Which kind of clay? Red clays, as was the case in Italy, or white ones?

The colour of the clay is of no importance, except for the side effects of MnO_2 in colouring, while everything depends on the level of impurity in the clay.

In Spain, where red-firing clays make up about 90% of wall and floor tile manufacture, only one part of the plastic clays (vitrifying) has a significant amount of organic matter, whereas the white clays generally give rise to more problems.

- What kind of body preparation? Spray-drying or extrusion?

The extrusion process is used in 10 Spanish companies, with an output of less than 15 million m^2 tile out of 300 million m^2 tile, i.e. a marginal proportion which presents more black core problems than the spray-dried powder sector, although the latter is not wholly free of the problem either because of currently employed firing cycles or the effect of the glaze.

b) The situation tomorrow may be somewhat different, in view of the efforts being made in optimizing productiveness and reducing firing time.

Although it is certainly true that firing cycles for spray-dried powder compositions have dropped strikingly, with some companies operating at 30/35 min, many lie in the 40/45 cycle, black core being one of the parameters that has impeded even greater production yield.

Control of cooling and glaze stability are other parameters - which are not insurmountable - that restrain greater productiveness (as well as insufficient dryer capacity in extruding facilities).

In Italy in particular, studies have been carried out on reducing firing time even further, to about 25 min. There could be a potential acceleration in firing of up to round 40% in respect of the current 40 min firing schedule found in many companies.

Treating black coring will be a priority subject in attempting to raise productiveness.

2) SIDE EFFECTS ON USING PYROLUSITE FOR REDUCING BLACK CORING

2.-1 Negative aspects or side effects requiring correcting measures

a) Other more urgent priorities of the trade. With a booming industry, the subject of black coring, although an issue on the mind of ceramists, is obviously not a matter of prime concern. Several tests were postponed for this reason.

b) Flashing: though not actually due to MnO_2 itself, the initial change in various parameters (clays-grog, etc.) at the commencement of testing gave rise to this phenomenon.

c) Bubbles in the glaze. Although in theory possible with the second small point of oxygen release between

1000 and 1100°C, this remained unconfirmed in practice owing to the low addition amount involved (0.5-1.5% pyrolusite). If required, two solutions would be to use slightly more refractory glazes (above 1100°C), or employ an additive with MnO_2, whose workings have already been tested (cf. Annex 3).

d) Unsuitable colouring. Although at 1% in fast firing it remains hardly noticeable in white bodies and slightly more in redware.

e) Above all, the hesitation stems from it being a rather unfamiliar process, while other possibilities are today available - which will likely turn out to be inadequate tomorrow with faster firing cycles - such as better regulation of the firing operation, use of natural gas instead of fuel oil, optimized clay preparation, and slower average real firing cycle than kiln capacities would actually allow.

2.-2 Positive side effects

a) The main one is undoubtedly the marked drop in the coefficient of water absorption. The tests run at 1.5% as well as a low level of 0.5/0.7% yielded a reduction that was almost equivalent to the pyrolusite percentage addition. It may be easier to meet the requirement set out in the standard on frost resistance for ceramic tiles, with 0.5% or 1% less water absorption for ceramists working close to the limits laid down in the standard.

b) Drop in the grog percentage when they are used in particular in the extrusion process, to enhance outgassing. However, a marked decrease in grog content, unaccompanied by better use of non-plastic clays, may give rise to increased flashing.

c) Energy saving (already found in structural ceramics with an economy of 20-40°C on using 2-3% of a product that was less reactive than micronized pyrolusite).

d) Strength or thickness of floor tiles. This is a direct consequence of reducing black core, which would enable the thickness and strength of large floor tiles to be increased, if this were to be targeted. Trials were run on floor tiles that were 11 and 12 mm thick (see slides).

e) Possibility of a wider selection of clays, in view of their properties or proximity, in spite of containing organic matter. More sandy or siliceous clays might also be employed, owing to the fluxing character of pyrolusite.

3) ECONOMIC BALANCE

According to the criterion, the additional expenditure could go, for an average use of 1% UFM 80, from 70% of the cost of clay in situ, to 1% of the floor tile sales price (see Annex 6).

CONCLUSION:

Laboratory tests and recent industrial trials (although the treatment of black coring with pyrolusite from IMINI, using less processed products than those of today, has long been applied in Italy), the conclusion may be drawn that micronized pyrolusite provides a technically and economically viable way of treating the problem of black coring and enhancing (particularly with regard to the coefficient of water absorption) the characteristics of the ceramic product.

This does not mean that there may not be other ways, which are currently more proven, as well as the need for adapting to the side effects. However, the stricter quality standards are, and the higher productiveness is, the wider will the range of applications for micronized pyrolusite be in fine ceramics, and perhaps in certain areas of structural ceramics. The IMINI mine is ready to attend to this demand for selected products such as concentrated and micronized pyrolusite.