THE USE OF MICRONISED PYROLUSITE (βMnO_2) IN FAST FIRED CERAMIC TILES

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1. INTRODUCTION

Natural ground manganese ores were originally used by ceramic brick and tile manufacturers to adjust the finished color in a range of grey to browns to black in combination with red clays. With the increase in firing cycles and fast firing technology, βMnO_2 or pyrolusite may also be used to improve in-process and final characteristics of the ceramics produced.

Over the past several years we have been studying the effects of small (0.1% - 4.0%) additions of pyrolusite (βMnO_2) produced by the SACEM at their mine located in IMINI (Morocco), on the structure of ceramic tiles and bricks. Our research has focussed on helping manufacturers minimize problems linked to the presence of organic materials in clays, these problems are increased by the use of fast firing technology.

2. CRYSTAL STRUCTURE OF βMnO_2 (PYROLUSITE) AND LABORATORY TESTS

Manganese ores consist principally of impure hydroxides and dioxides in a variety of mineral structures and crystal forms. The beta phase, represented by the mineral pyrolusite, βMnO_2 is characterized by a high degree of crystallinity and an almost perfect stoichiometric composition.

SEM analysis shows the acicular (needle like) structure of the pyrolusite crystals. The pyrolusite crystals are present as individual needles in sizes between 30μm and 150μm (100μms on average) in length, 1μm to 2μms in diameter. In addition to the needlelike grains, 2 other forms are present; one with an angular structure with equivalent diameters of up to 20μm, and in lesser quantities a spheroidal grain with an average grain size of 5μm associated with Psilomelane.

Laboratory studies were made on a range of fine (0 to 80 μm), and ultrafine micronised (0 to 30 μm) from the SACEM's mine at IMINI in Morocco. The samples were mainly pyrolusite bearing. The purities ranged from 70 to 92% MnO_2. Different samples were used to determine the optimum powder for black core reduction. This optimum was found to be an ultrafine micronised (UFM) material with 80% MnO_2 content. With the ultrafine micronised 80% MnO_2 as little as a 2% addition of the powder was sufficient to eliminate black cores in clays with organic compounds of 0.5 to 1% in a fast firing cycle (40K/minute) under laboratory conditions.

3. INDUSTRIAL TESTS WITH MICRONISED PYROLUSITE

After the positive results of laboratory tests, the effects of small additions of pyrolusite on the behavior of the ceramic body was examined on an industrial scale. Several of our Spanish customers have given us data to demonstrate the effects they found industrially when using UFM 80 (ultrafine micronised 80% manganese with a high pyrolusite content).

a. Industrial Conditions and Results

Industrial Conditions:

Product:	One standard stoneware formulation
Size:	45 * 45 * 9
Firing cycle:	37.40 minutes
Furnace length:	109 meters
Furnace entry:	2070 millimeters
Production:	4300 m^2/day
Temperature profile:	A maximum temperature of 1145° is reached at 60% of the furnace length.

A Spanish stoneware formulation containing red clays was used as a basis for comparison. The stoneware formulation used was 77% Villar clay with a low, <3%, carbonate content, containing organics. The Villar clay was mixed with 23% San Juan Moro without organics. UFM 80 was added to this clay formulation. The base case achieved the required density at 5.8% linear contraction which corresponds to a firing temperature of 1140° under the conditions described above. An addition of 0.2% UFM 80 reached the same linear shrinkage at 1125°, a reduction in firing temperature of 15°. An addition of 0.3% UFM 80 further reduced the firing temperature by 15° to 1110°.

The fired tiles were slightly darker in color than the standard formulation, around 10%, and showed no black core defects.

Table 1 shows the standard parameters for water absorption and linear shrinkage as compared to the results obtained with the 0.2% and 0.3% addition of UFM 80. The linear

shrinkage percentage was held constant to determine the maximum firing temperature required to obtain the same shrinkage/density.

	% Water absorption at 1140°	% Linear shrinkage at Firing T°	Firing Temperature °C
Stoneware tile w/o MnO2	4.0%	5.8%	1140
Stoneware tile w 0.2% UFM 80	3.2%	5.8%	1125
Stoneware tile w 0.3% UFM 80	3.0%	5.8%	1110

Table 1. *The effect of UFM 80 additions on stoneware tiles.*

Other industrial tests have shown that in general when firing tiles of 9 to 11 mm in thickness, the firing cycle can be reduced by 10% with an addition of less than 0.5% of UFM 80. This implies that firing cycles of 35 to 40 minutes can be reduced to 31 to 36 minutes. The reduction in firing cycle is possible due to the oxygen released by the pyrolusite which accelerates organic burnout yielding dense bodies without black core defects.

b. Other effects of manganese additions

Color: Small additions (0.1 - 4.0%) of fine and ultrafine micronised (UFM) MnO_2 to bricks and tiles made from red clay under normal firing cycles yield brown tints. This color effect is much deeper with with UFM 80 due to the higher reactivity of the micronised powder. Very small percent additions have significant coloring effects. With white clays the effet is even more pronounced. Fast firing cycles, however, totally change the effect. White clays show little coloration and no generalisation can be made concerning red clays.

Porosity: Manganese with a high percentage of pyrolusite is also an excellent flux. With most clays a 1% addition of pyrolusite will reduce the porosity by 1%. At the same percent porosity the firing temperature may be reduced providing energy savings.

4. CONCLUSIONS

Depending on raw materials, furnace type, the production/productivity requirements, MnO_2 in the form of micronised pyrolusite UFM 80 can provide many options for optimising the manufacturing process. The addition of small percentages of UFM 80 results in:

a) the ability to use clays with higher organic contents 0.5% to 1.0%.

b) a reduction in the water absorption between 1050° and 1150° allowing the use of more refractory clays and easily meet anti-freeze standards.

c) a reduction in the firing temperature of 15° to 30° and a decrease in the cycle time of 5% to 10%.

d) improved microstructures in fast fired tiles of 9 mm thickness, even with very small additions (<0.3%), and for thicker tiles with higher additions.

The laboratory research and subsequent industrial tests performed over the last

several years demonstrate that micronised pyrolusite UFM 80 (MnO_2) enhances many aspects of tile and brick manufacture in addition to its known coloring effects. Research is continuing in industrial settings to further confirm our results and extend our knowledge through tests with a variety of ceramic raw materials commonly used in Spain in existing conditions in ceramic plants which could benefit from the introduction of UFM 80.