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Recycling the insoluble residue from titania slag dissolution (tionite) in clay bricks

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Abstract

Tionite is the insoluble residue from the titania slag dissolution process for TiO₂ manufacturing. It is a fine grained sludge consisting of rutile, anatase, amorphous phase and bassanite. Chemical composition is TiO₂ (ca. 50%), SiO₂ (ca. 30%) and minor Al, Ca, Mg, and Fe, plus residual sulfur, implying an acidic pH of waste. Moisture is about 35% of dry weight. The potential of tionite as colouring agent in clay bricks was appraised by admixing (up to 9%) either as-produced or neutralized tionite to four industrial clay bodies. The effect on technological behaviour was assessed by laboratory simulation of the industrial brickmaking process and determining working moisture, drying sensitivity, shrinkage and bending strength, water absorption, bulk density, efflorescence, and colour. The use of tionite is technologically feasible, with little adjustment of industrial cycle, and resulting brick performances depend remarkably on the composition and properties of clay bodies. Carbonate-rich bodies seem to be affected by tionite more during drying than during firing; carbonate-poor bodies range from little changes to consistent worsening of brick performances. No relevant changes of process and product parameters were found up to 3% tionite. Additions over 5% induce significant variations, such as increase of working moisture and water absorption, decrease of bulk density and bending strength. A definite and consistent improvement of this technological behaviour is achieved by using neutralized tionite. The yearly output of tionite could be entirely recycled by approximately four average size brickworks adding about 3% of residue (dry weight).

Key words: Ceramics, Clay brick, Tionite, Titania slag, Waste recycling.

1. Introduction

Pigment grade TiO₂ is recovered from Ti-rich slag by chemical processes [1] among which acid dissolution in H₂SO₄ [2]. Ti-rich slag is obtained by a smelting process, conducted at about 1600 °C, of Ti ores admixed with coal [3-4]. The slag – obtained by decrepitation [5] – is mostly vitreous and contains Ti, Fe, Mg, Ca, Al and Si as major components along with minor elements like Mn, V, Ba, Cr, Co [6-9].

Even if the processing of Ti-rich slag is carried out with high yield, a certain amount of insoluble residue is left in the form of blackish paste, named 'tionite' [10], which is classified as special material due to its low pH consequent to the occurrence of residual acid from the sulphidation process. Tionite is currently disposed in landfill with increasing difficulties and cost, so urging industry to find a recycling way for it. However, a large-scale re-use is hard to be envisaged for the peculiar chemical and physical properties of tionite,

which needs a neutralization treatment (by adding calcium hydroxide in almost stoichiometric amount to H_2SO_4 to form gypsum).

Although recycling is documented for a wide range of wastes from metallurgical and allied industries [11-13], nothing is known in the literature about reutilization of Ti-rich residues. Tionite is claimed to be introduced in clay bricks [14] but no detailed study has been undertaken till now to assess actual potential and limits of this recycling route.

This paper is aimed at appraising the re-use of tionite in brickmaking, addressing key-points in processing and product performance. The rationale consists in adding growing waste amounts to four different types of industrial clay bodies, testing their technological behaviour at the laboratory scale and characterizing semi-finished and finished products in order to assess technological feasibility and estimating the best amount of tionite actually recyclable.

2. Experimental

The waste was sampled from the Tioxide Europe plant in Scarlino (Tuscany, Italy) in two forms: as-produced tionite (apT) and neutralized tionite (nT) by $Ca(OH)_2$ addition. Tionite was characterized by chemical analysis (XRF-WDS), phase composition (XRPD, Rigaku Geigerflex), particle size distribution (X-ray monitoring of gravity sedimentation, Micromeritics, SediGraph 5100) and thermal behaviour (hot-stage microscope, Expert System Misura 3).

Four clay bodies were selected as representative of the production of clay bricks and blocks in Tuscany [15-16]. These bodies were characterized determining chemical composition (XRF-WDS, Philips, PW 1480), mineralogical composition (XRPD, Rigaku Geigerflex), particle size distribution (Micromeritics, SediGraph 5100). Samples D and Y are carbonate-rich batches, while bodies N and R are poor in carbonates (Table 1); particle size distribution is rather fine-grained for body N, relatively coarse-grained for body D, intermediate for bodies R and Y (Fig. 1).

Four series of clay/waste mixtures were designed, adding to each body 0%, 3%, 6% or 9% (dry basis) of apT (samples D, N, R and Y) or nT (samples D*, N* and R*).

The technological behaviour of these batches was assessed during body preparation, shaping, drying and firing through a simulation, on a laboratory pilot line, of the industrial processing of clay bricks. In particular, the following working phases were carried out:

- (i) clay grinding with a jaw crusher (<20 mm) and a hammer mill (<1 mm);
- (ii) hand mixing of clay, tionite and water, and successive storage for 7 days;
- (iii) plastic extrusion of 100 x 20 x 10 mm³ bars, with a pneumatic apparatus without vacuum;
- (iv) drying at ambient temperature in non-controlled atmosphere for 48 h and then in electric oven at 100 °C overnight;
- (v) firing in electric chamber kiln, in static air, following the firing schedule of each industrial kiln (maximum temperature of 920 °C for body D, 970 °C for bodies N and R, 1060 °C for body Y, thermal rate of 100°C/h, 4h soaking).

Unfired and fired products were characterized determining:

- working moisture (ASTM C 324);
- drying and firing shrinkage (ASTM C 326);
- modulus of rupture of dry and fired samples (ASTM C 674);
- drying behaviour with Adamel apparatus on 80x20x10 mm³ moulded bars; the drying process is characterized by weight loss occurring in two stages (W1 with shrinkage and W2 without shrinkage) that are graphically represented by the Bigot's curve; a drying

sensitivity index was calculated as $DSI = W_1 \cdot \text{drying shrinkage} \cdot 0.01 / \text{dry modulus of rupture}$ [17];

- water absorption, open porosity and bulk density of fired samples (ASTM C 373);
- efflorescence of fired samples (ASTM C 67);
- colour (Hunterlab Miniscan MSXP4000).

In order to make easier comparison and interpretation, data from all series are plotted in a single graph for each technological variable, having care to normalize and express results with respect to the relevant waste-free body (whose value = 1.00).

3. Results and discussion

3.1. Chemical and physical properties of tionite

Tionite has a very selected and fine particle size distribution, being for over 80% in the 1-20 μm range (Fig. 1). It consists of titanium dioxide (rutile and anatase), calcium sulfate hemihydrate (bassanite) plus an abundant amorphous phase (Fig. 2).

The chemical composition of tionite is characterized by predominant TiO_2 (~50% on dry basis) and SiO_2 (~31%) plus minor amounts (2-4%) of Al, Ca, Mg, and Fe oxides; moisture is close to 35% of dry weight (Table 2). The occurrence of residual sulfur (~6%), implying an acidic pH, along with significant amounts of Mn and V (>1000 ppm) plus Ba, Cr and Co in contents over 100 ppm, turns tionite into a hazardous material. The neutralization treatment, carried out adding $\text{Ca}(\text{OH})_2$ in nearly stoichiometric amount to SO_3 , shifts pH to approximately 7.

Firing behaviour is characterized by a substantial stability up to ~900 °C (Fig. 3) followed by sintering (~1200 °C), bloating (~1300 °C) and melting (>1400 °C).

3.2. Technological behaviour of clay bodies

The introduction of tionite into clay bodies did not induce remarkable changes of technological behaviour during laboratory simulation of brickmaking process. In most cases, differences turned to be appreciable only comparing the relevant physical characteristics.

Once tionite is added, a greater amount of water is needed to extrude all kinds of bodies. Such increasing is proportional to the percentage of waste added, reaching values of 10-15% more in the case of 9% nT, even though 3% addition causes an increment of just 4-7% relative (Fig. 4) that, in terms of water consumption, corresponds to an increase of 1 to 1.5 kg every 100 kg of body.

The greater amount of working moisture implies lower density of semi-finished products, as bodies are water-saturated during extrusion and so evaporation leaves a larger percentage of porosity. This affects the mechanical resistance of dry bricks, that is gradually lowering when tionite percent increases. Such deleterious effect – inducing 15% to 30% of bending strength reduction for 6-9% apT – is subdued using neutralized tionite (Fig. 5): additions of 3-6% nT may cause a drop of dry bending strength in the 2-17% range, corresponding to a strength of 3.5-5 MPa, thus fulfilling usual requirements in the industrial practice [17].

The drying behaviour is influenced by the type of tionite and clay body. As-produced tionite provokes strong changes in non-carbonatic bodies (turning more sensitive to drying by a 30-40% with 3% apT, besides fading for increasing additions) but, in contrast, causes negligible or even beneficial effects in carbonatic bodies (Fig. 6). Such fluctuations are effectively dampened adding neutralized tionite, although the different behaviour of

carbonate-rich and carbonate-poor bodies is confirmed. The addition of 3% nT does not significantly affect the drying sensitivity.

Total shrinkage occurring during drying and firing replicates the tendency of carbonate-poor bodies to be more influenced by the presence of tionite than carbonate-rich ones do (Fig. 7). Using the neutralized waste, variations in the final size of bricks is in most cases in the 0-5% range, corresponding to less than 0.5 cm/m.

3.3. Technical performance

Technical characteristics of finished products vary in a rather proportional way to the waste addition; the use of neutralized tionite gave in most cases beneficial effects, by reducing the entity of changes and the overall difference among the various clay bodies.

Adding tionite implies increasing water absorption (Fig. 8) and decreasing bulk density (Fig. 9) whatever kind of body is concerned, although variation ranges are narrower in carbonate-rich formulations. Such increasing is in the 3-6% range with 3% nT, corresponding to 16-18% wt. of water absorption more, anyway within standard values.

The reduced density of tionite-bearing bricks brings about a lower mechanical resistance with no appreciable distinction on the basis of carbonate content (Fig. 9). Once neutralized tionite is introduced at 3%, bending strength is lowered by a 2-10%, attesting on values in the 11-13 MPa. Even if waste addition as high as 9% may drop the strength by a 25%, the actual strength of 9-12 MPa which fulfils standard requirements.

Colour changes may be from negligible to conspicuous with no apparent relationship with body type (Fig. 10). However, the use of neutralized tionite is able to limit such variations, minimizing the chromatic change with 3% waste addition, although with larger amounts the hues result rather variable.

One expectable drawback from the introduction of tionite into brick bodies concerns efflorescence, due to the remarkable sulfur contribution as either partially calcium sulfate (apT) or entirely calcium sulfate (nT). The results obtained are to a certain extent surprising, since the increased S content in carbonate-rich bodies (Y) or S-rich bodies (D) does not translate into enhanced efflorescence, but may have even some beneficial effect (Fig. 11). Carbonate-poor and S-poor bodies, in contrast, tend to manifest a stronger degree of efflorescence when the addition of apT or nT is increased. This may be the most critical point, although addition of 3% nT gave rise to limited changes, e.g. from weak to medium degree of efflorescence, anyway complying standard requirements.

3.4. Recycling prospect

On the basis of technological behaviour and technical performances, the maximum amount of neutralized tionite that can be recycled, without unacceptable effects, is 3% weight (dry basis) corresponding to approximately 4% weight of the wet material. No change in the brickmaking process is required; the only additional equipment is a box feeding device for dosing tionite.

In the case-study of the Scarlino plant, from 15 to 20 thousand tons per year of tionite are produced, which may be, once properly neutralized, entirely utilized in the clay brick manufacturing cycle. Since the recommended tionite amount recyclable is 4%, it implies that a yearly output of 20,000 tons needs approximately half million tons of clay body for its safe incorporation. Considering that the average size of Italian brickworks make use of around 150,000 tons of body per year, the global amount of tionite can be recycled by 3 to 4 plants.

A key-point for the economic viability of waste recycling is transportation cost, according to which the distance from titania manufacturer to brickwork should not exceed 100-150 km. In the case-study, there are 8 brickworks within this radius.

4. Conclusions

Recycling of titania-rich wastes, like the insoluble residue from titania slag acid dissolution (tionite), in brick bodies is technologically feasible with little adjustments to industrial manufacturing. The effects depend on the waste treatment (as-produced or neutralized tionite), the amount added and the characteristics of clay body.

Neutralization of residual acidity allows a consistent improvement of tionite technological behaviour, essentially related to the proper pH value, mostly manifested by a narrower variation range in function of both the percentage of residue and body type.

Additions up to 3% (dry basis) induce tolerable changes of processing parameters or product performance. Contents over 5% tionite bring about significant variations, mainly concerning increasing working moisture and water absorption as well as decreasing bulk density and mechanical strength.

Tionite-bearing, carbonate-poor bodies exhibit a range of technological behaviours – going from little change to remarkable worsening of brick performance – wider than carbonate-rich bodies, which seem to be mostly affected in the drying stage.

The yearly output of tionite by a titania manufacturing plant (in the present case-study ~20,000 tons) could be entirely recycled – once neutralized – by approximately four average-size brickworks adding 4% wt. (wet basis) of residue to the clay body.

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Table 1
 Composition of clay bodies.

wt. %	D	N	R	Y
SiO ₂	51.6	59.9	63.7	46.0
TiO ₂	0.5	0.6	0.6	0.6
Al ₂ O ₃	12.0	14.3	14.8	13.1
Fe ₂ O ₃	3.9	4.9	5.1	4.6
MgO	2.3	2.5	2.9	3.9
CaO	11.2	4.7	2.2	12.5
Na ₂ O	1.2	1.0	1.6	1.2
K ₂ O	2.4	2.3	2.6	2.8
S	0.6	<0.1	<0.1	<0.1
L.o.I. (1000 °C)	12.9	9.0	6.3	15.1
Quartz	31	36	34	25
Calcite	17	8	3	16
Kaolinite	6	13	1	traces
Feldspars	10	8	20	12
Smectite	traces	traces	12	1
Illite	20	19	19	25
Chlorite	4	10	8	11
Dolomite	6	traces	traces	7
Fe-oxyhydroxides	3	2	3	3
Accessories	3	2	traces	traces
>63 µm	24	14	32	13
>20 µm	35	23	42	26
<4 µm	43	56	43	50
<2 µm	31	43	37	37

Table 2
Chemical composition of tionite.

Major components (wt.%)	Wet basis	Dry basis
Moisture at 105 °C	26.6	0
SiO ₂	21.08	31.07
TiO ₂	34.09	49.89
Al ₂ O ₃	2.57	3.79
FeO	1.39	2.11
MgO	1.63	2.40
CaO	2.48	3.54
MnO	0.29	0.42
K ₂ O	0.30	0.44
S	4.30	6.33
Minor components (ppm)		
As	< 2	< 2
B	9	12
Ba	477	650
Be	3	4
Cd	< 0.5	< 0.5
Co	173	236
Cr	378	515
Cu	72	98
Hg	1	1
Mo	2	2
Ni	7	10
Pb	13	18
Sb	5	7
Se	1	1
Sn	1	1
V	796	1085
Zn	8	11

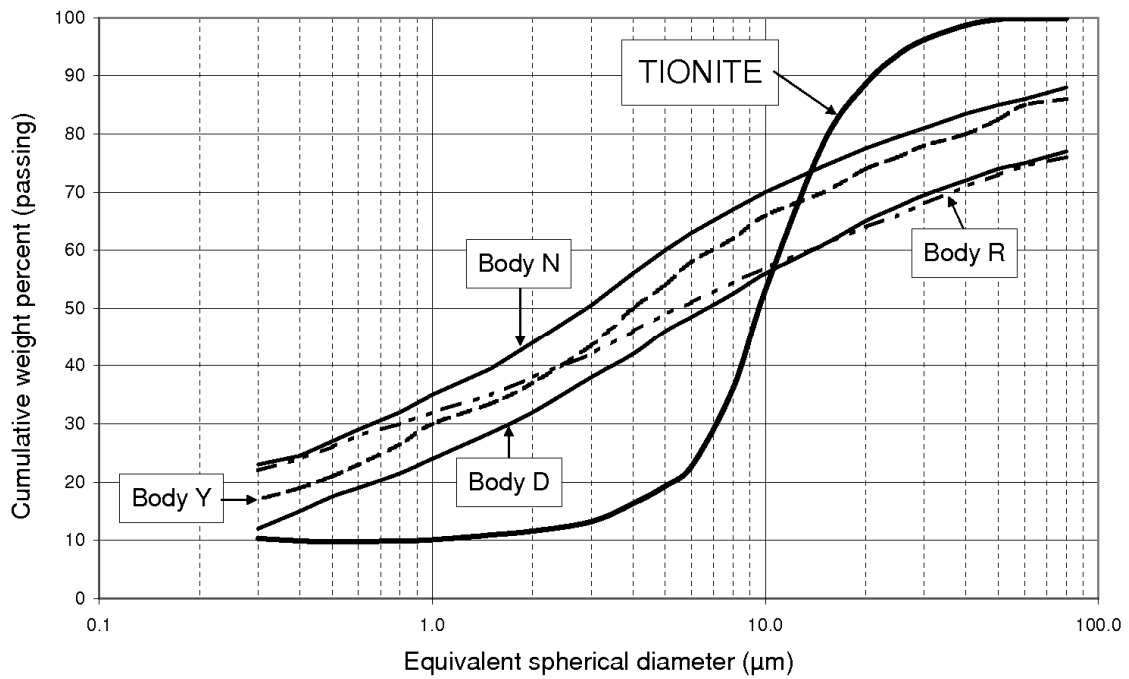


Fig. 1. Particle size distribution of tionite and clay bodies.

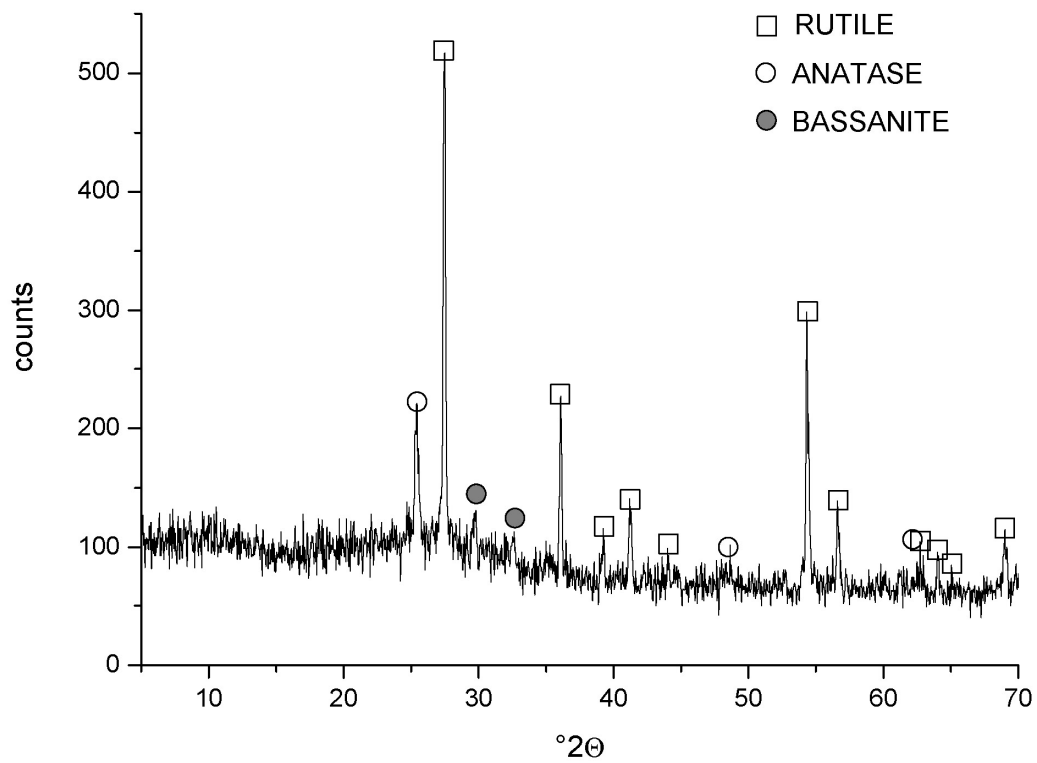


Fig. 2. X-ray diffraction pattern of as-produced tionite.

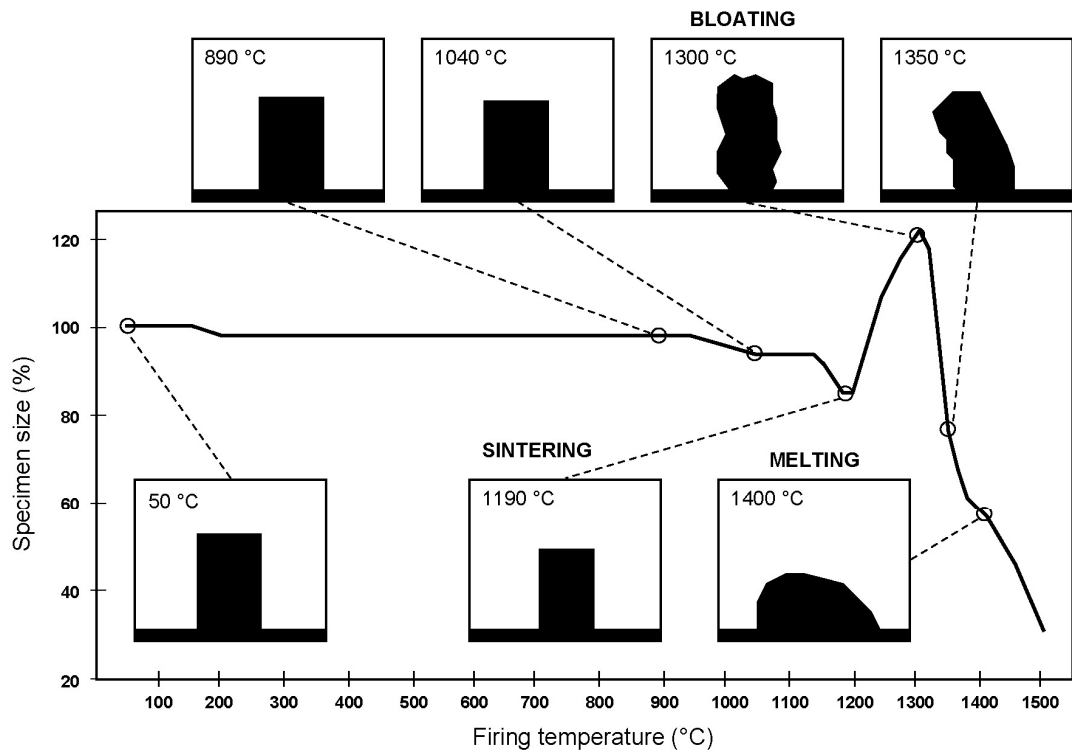


Fig. 3. Firing behaviour of tionite under hot-stage microscope

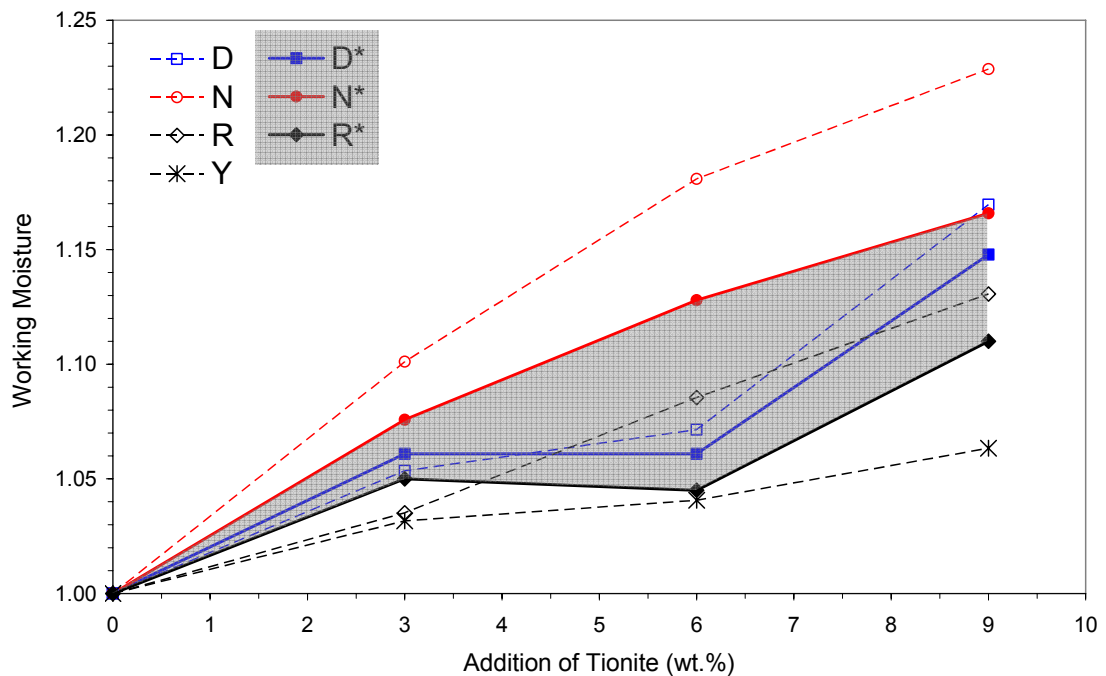


Fig. 4. Effect of tionite addition on working moisture of clay bodies (asterisk and gray field = neutralized waste)

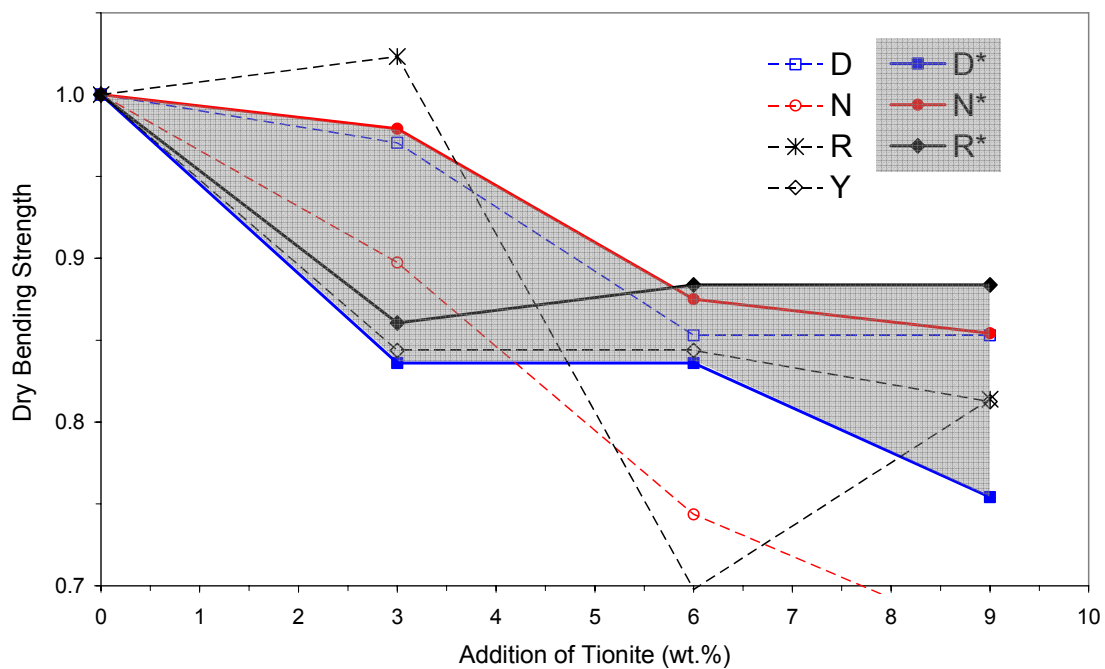


Fig. 5. Effect of tionite addition on dry bending strength of clay bodies (asterisk and gray field = neutralized waste)

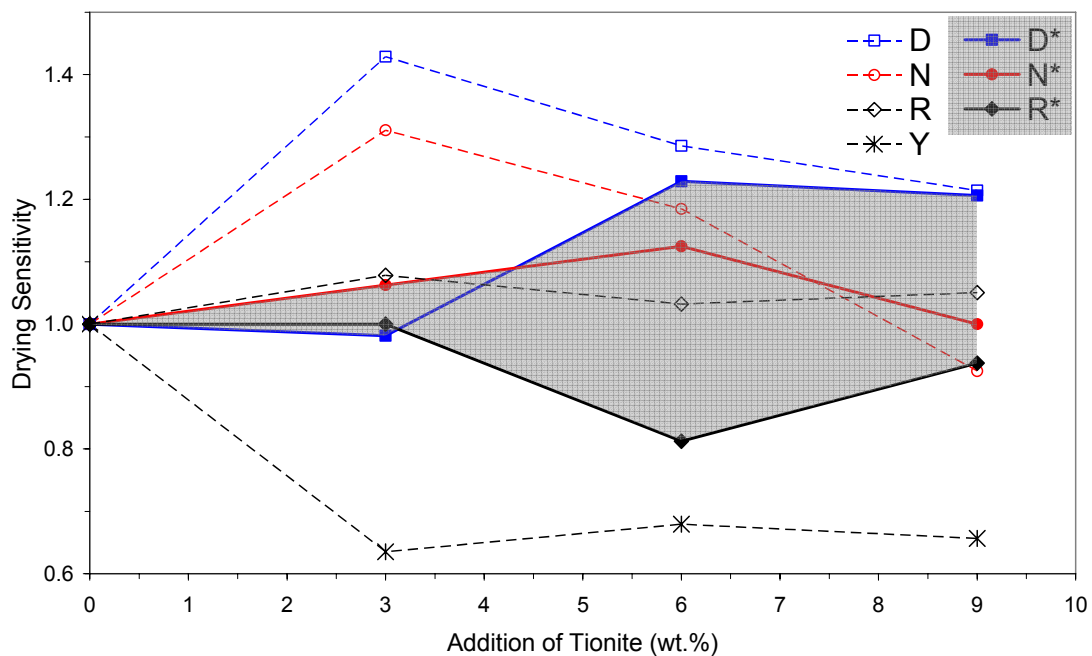


Fig. 6. Effect of tionite addition on drying sensitivity of clay bodies (asterisk and gray field = neutralized waste)

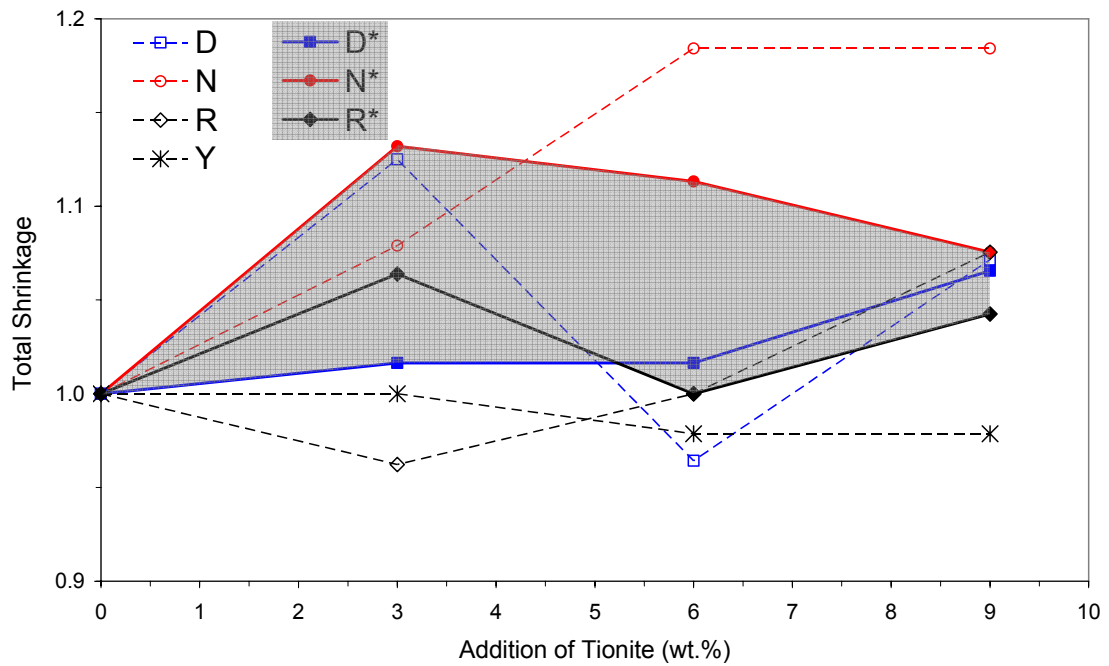


Fig. 7. Effect of tionite addition on total (drying+firing) shrinkage of clay bodies (asterisk and gray field = neutralized waste)

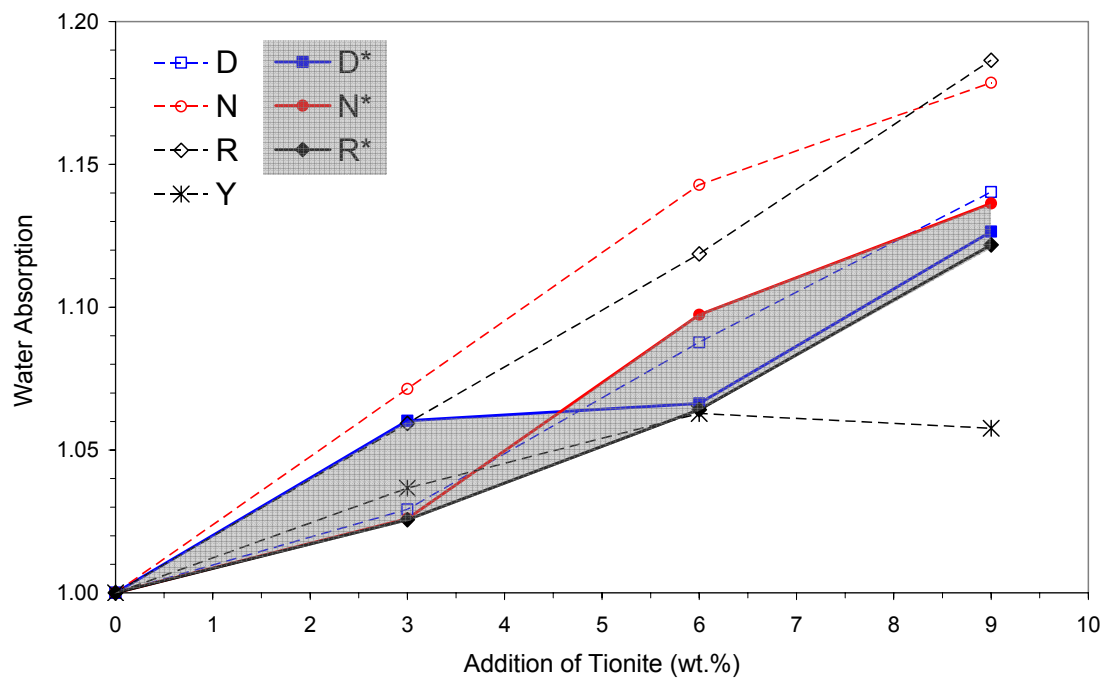


Fig. 8. Effect of tionite addition on water absorption of fired bodies (asterisk and gray field = neutralized waste)

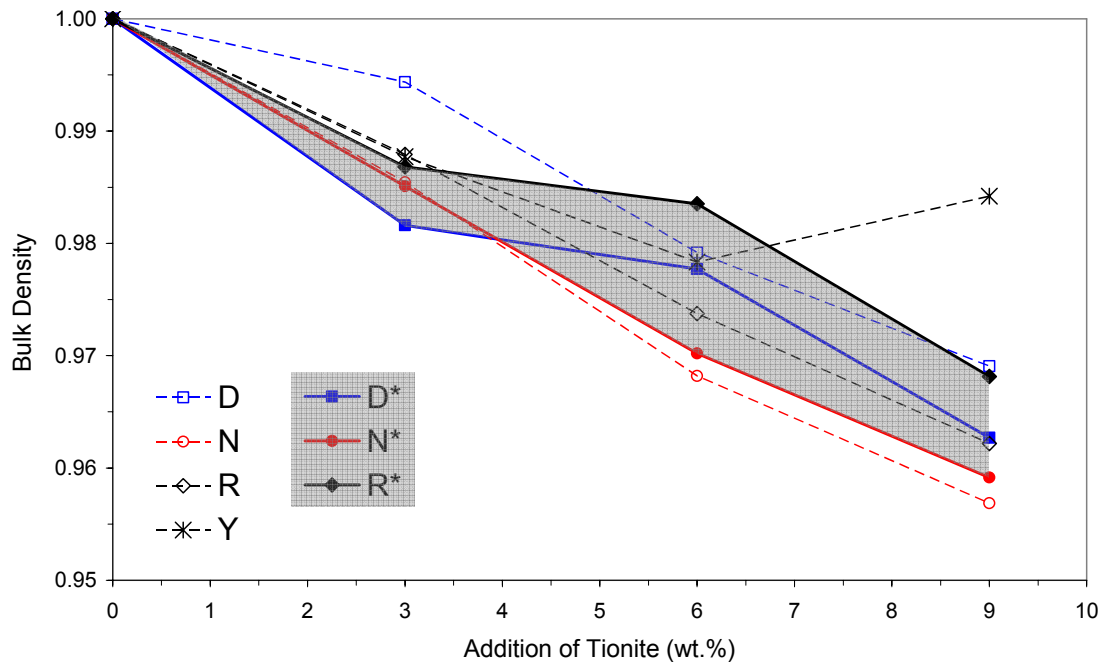


Fig. 9. Effect of tionite addition on bulk density of fired bodies (asterisk and gray field = neutralized waste)

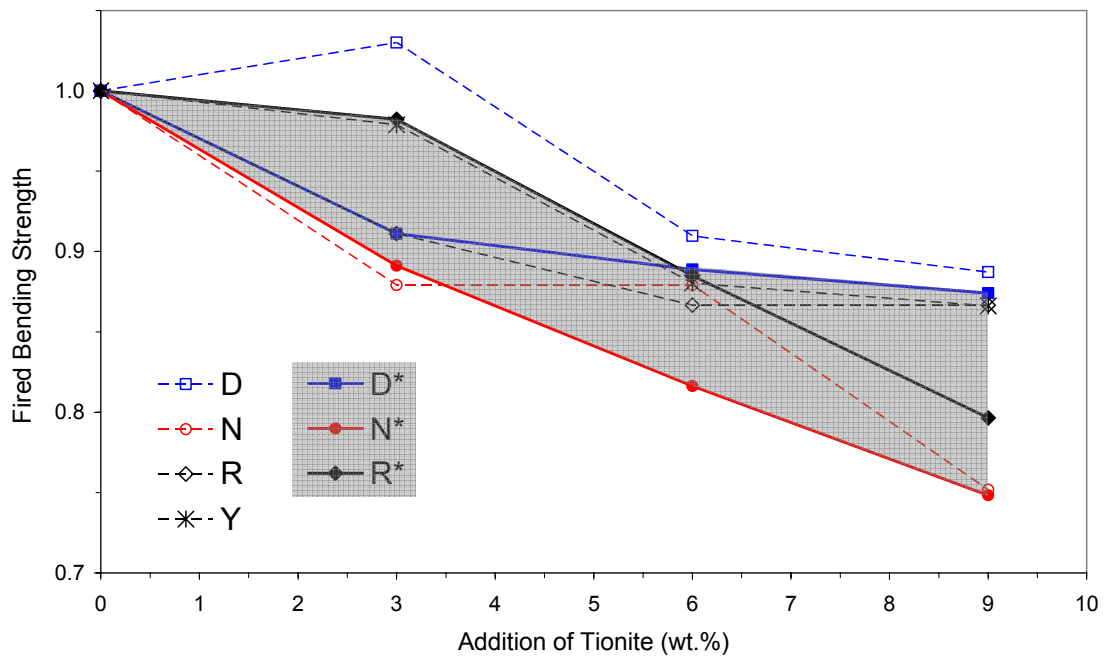


Fig. 10. Effect of tionite addition on bending strength of fired bodies (asterisk and gray field = neutralized waste)

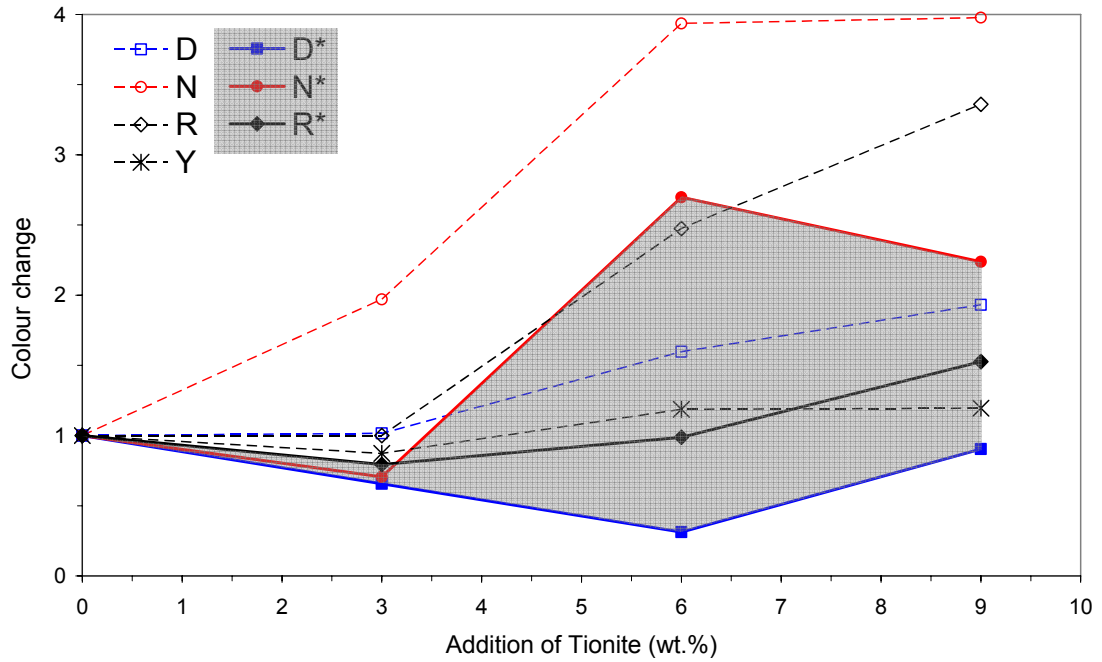


Fig. 11. Effect of tionite addition on colour of fired bodies (asterisk and gray field = neutralized waste)

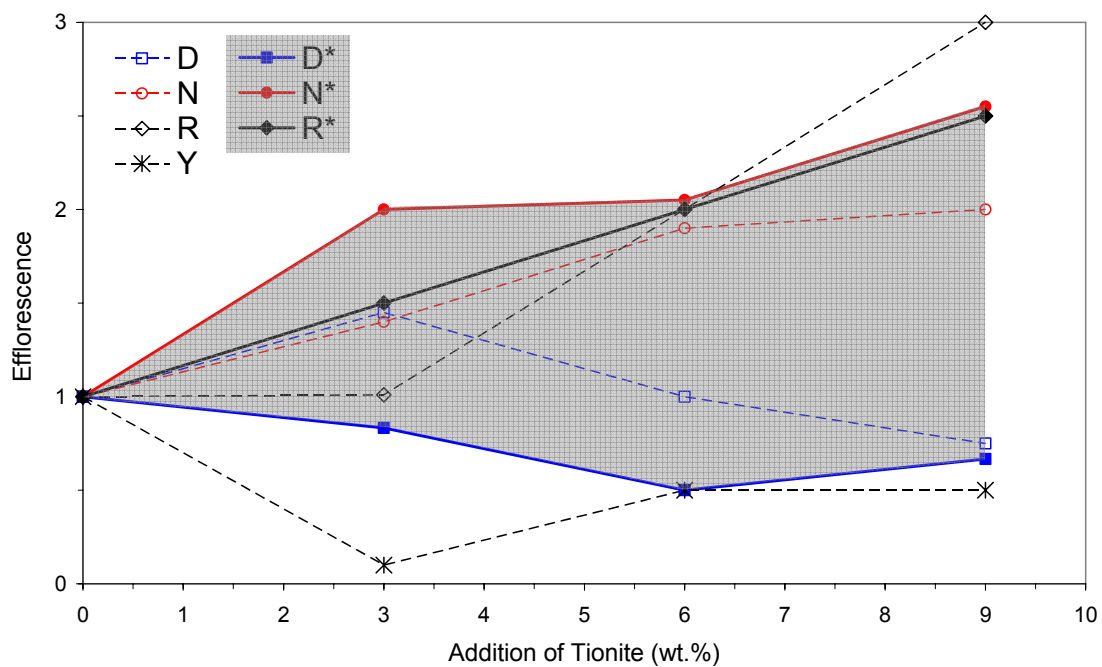
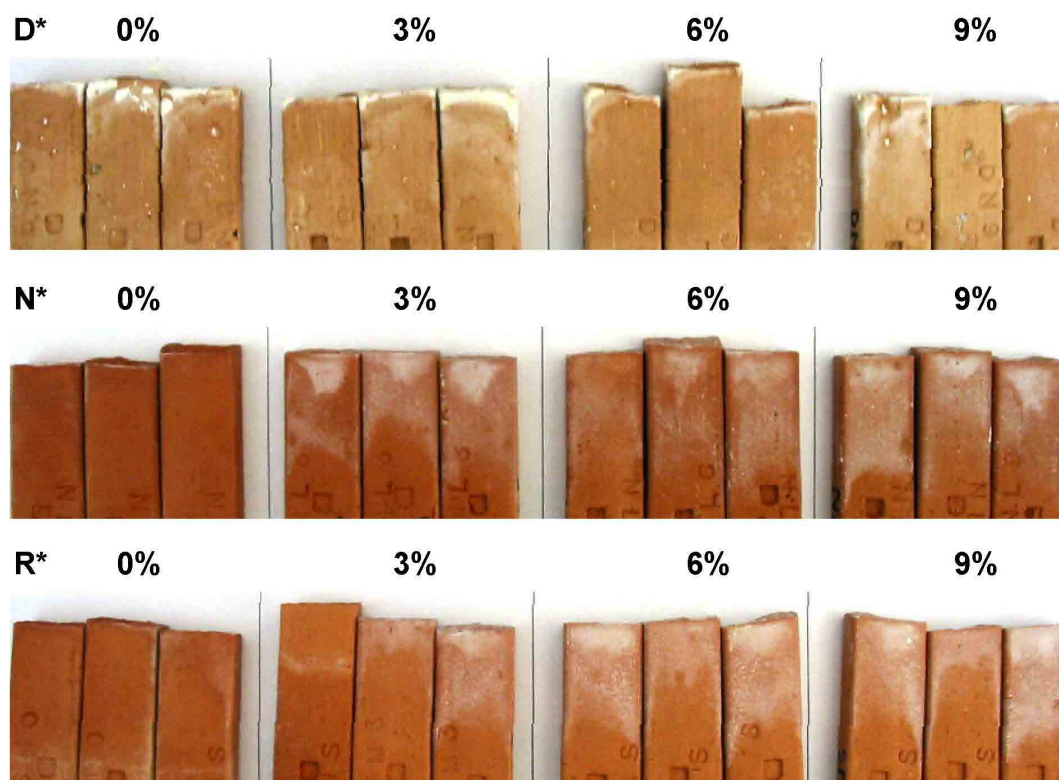


Fig. 12. Effect of tionite addition on degree of efflorescence of fired bodies (asterisk and gray field = neutralized waste)