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Titanium fume and ilmenite fines characterization for their use in cement-based materials

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Abstract

A series of characterization experiments was conducted to evaluate two by-products from the iron and titanium industry (ilmenite fines and titanium fume) to be use in cement-based materials. Although these by-products show a weak reactivity (early age), their physical properties, especially in the case of titanium fume, which is formed of spherical particles with a mean particle diameter of 1.7 μm, lead to an enhancement of the mechanical strength of mortars (for mortars containing up to 5% replacement of cement). For larger substitution rates, their efficiency coefficients stand between those of inert and pozzolanic materials. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Several types of mineral powders commonly used as cementitious materials, such as silica fume and fly ash, are industrial by-products. The benefits of such materials are mainly economical (reduction of concrete cost, except in the case of silica fume) and environmental (reduction of cement production and of mineral waste in landfill sites). Moreover, some industrial by-product may also offer significant technological advantages, especially improvement of concrete durability, due to their particular fineness and reactivity.

The aim of this work is to study two by-products obtained from the titanium and iron industry, known as titanium fume and ilmenite fines, which present some interesting properties for their use in cement-based materials.

2. Origin of the by-products

Ilmenite fines and titanium fume are by-products generated by the titanium slag and iron industries. Titanium slag, containing 80% of titanium dioxide, is commonly used for the manufacture of white pigment for paint, plastic, paper and fabrics. Metallic iron is used for the fabrication of gray cast iron, nodular cast iron and carbon steel.

The industrial process, which consists of transforming an ilmenite ($FeTiO_3$) ore, requires two stages of purification and reduction; each involving the formation of a by-product. The purification consists in enriching the ore by eliminating part of the impurities, mostly composed of plagioclase feldspars and sheet silicates (micas/illites and chlorites). This operation requires a crushing process, followed by magnetic and gravity separations of the ore and leads to the formation of a by-product dust called ilmenite fines.

The beneficiated ore is mixed with coal and melted in an electric furnace. The very high temperature in the arc furnace during the fusion of the ore (more than 1700°C) generates metal vapors that are evacuated with the gases produced by the reduction reactions. When cooled with water these vapors are transformed into a dust called titanium fume.

Fig. 1 summarizes the industrial process leading to the formation of the products and by-products and the mode of recovery of these by-products.

The enrichment and smelting of the ilmenite ore generate large quantities of by-products. These by-products, in

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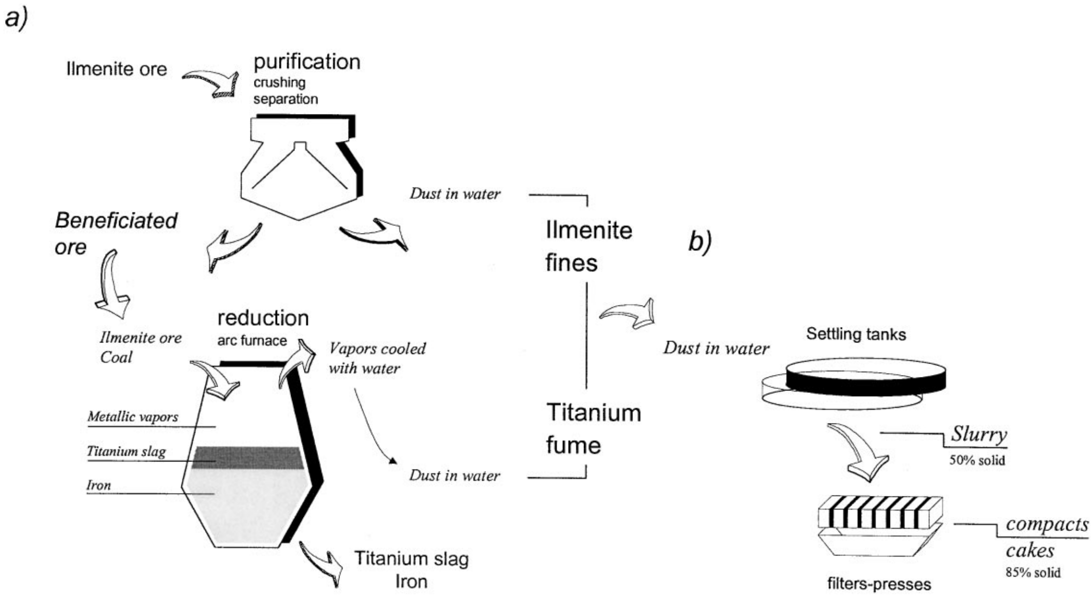

Fig. 1. (a) Industrial process and (b) recovery of the by-products.

water suspension, are transferred to a water treatment plant, where they are recovered, after a short stay in a settling tank. To reduce transportation costs, filter presses are used to produce cakes with a water content of approximately 15%. It is also possible to recover the mud before it enters in the filter presses. In that case, the slurry has a solid content of approximately 50%.

3. Physico-chemical characterization of the by-products

Although both ilmenite fines and titanium fume are produced by the same ore processing plant, they have quite different physico-chemical properties, due to their distinct modes of formation.

3.1. Physical properties

Ilmenite fines and titanium fume have a dark gray, almost black color, due to their variable contents of ilmenite and coal. Their densities are 3.76 and 2.92 g/cm^3, respectively. The lower density of the titanium fume is related to a vitreous phase, which has a lower density than that of metallic oxides composing the crystallized part of the materials.

The morphology of each by-product is controlled by its mode of production. As shown in Fig. 2a, the ilmenite fines, obtained by crushing, consist generally of angular grains. Their fineness approaches that of cement. The particles have an average diameter of approximately 25 μm, and their specific surface is around 1.5 m^2/g (BET).

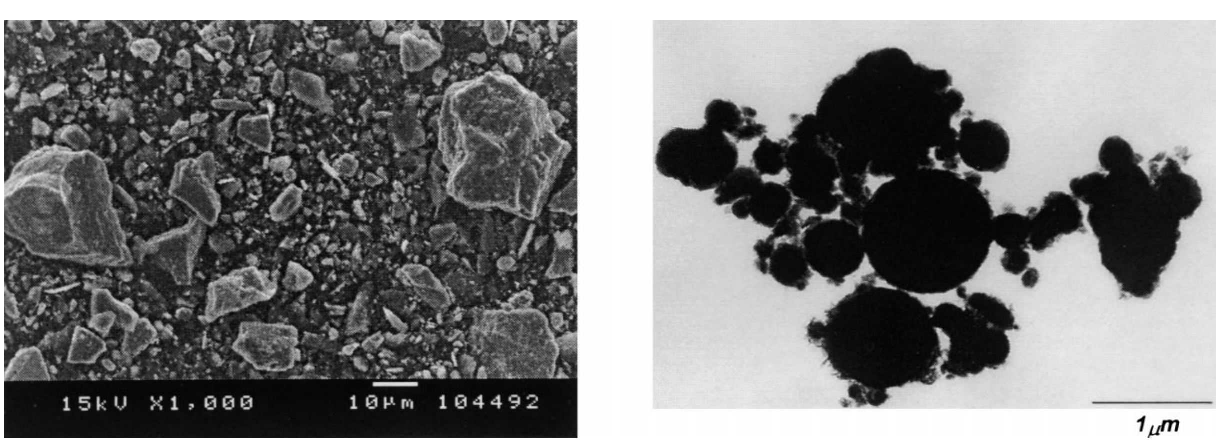

Fig. 2. Morphology of (a) ilmenite fines (SEM) and (b) titanium fume (TEM).

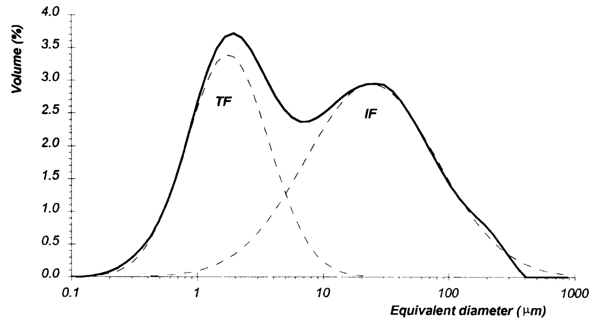

Fig. 3. Particle size distribution of a slurry containing ilmenite fines (IF) and titanium fume (TF), obtained by laser granulometry.

The morphology of titanium fume (Fig. 2b) appears as rounded particles and their distribution ranges from a few tens of nanometers to 10 μm, with a mean diameter of approximately 1.7 μm. The specific surface approaches 90 m^2/g (BET). The fineness of the titanium fume is much higher than that of Portland cement, which suggests a potential physico-chemical activity of the material in aqueous medium.

The particle size distribution of these by-products, measured by laser granulometry, is given in Fig. 3. The sample was a slurry-containing ilmenite fines and titanium fume in unknown proportions. The granulometric curve shows the existence of two populations of particles: the coarse fraction represents ilmenite fines while the fine part represents the titanium fume.

3.2. Chemical composition

The chemical compositions of the two by-products were determined by atomic absorption and are presented in Table 1.

3.3. Mineralogical composition

The XRD patterns show that ilmenite fines and titanium fume are quite complex materials having polyphasic structures. Ilmenite fines are exclusively composed of the same crystalline minerals that were already present in the ore and its impurities. The XRD patterns (Fig. 4) reveals the presence of ilmenite, geikielite, feldspars (plagioclases) and micas.

The titanium fume has a mineralogy that is directly linked to its mode of formation. The XRD patterns (Fig. 4) shows the existence of a significant vitreous phase, which are probably made of silicon, aluminium and alkali. In addition to ilmenite, the crystalline phases are mainly

Table 1
Average chemical analysis of ilmenite fines and titanium fume

	TiO_2	Fe_2O_3	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	CaO	LOI
IF	30	37	15	8	4	1	1	1	<2
TF	33	25	17	3	10	1	1	1	8

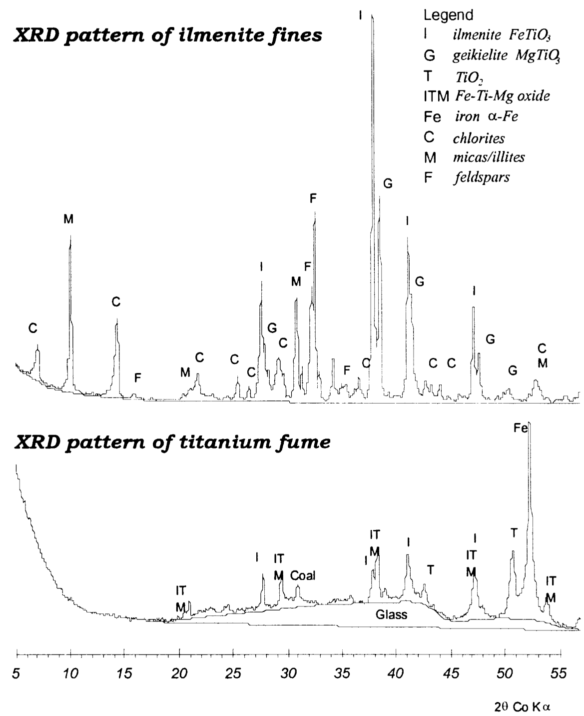

Fig. 4. Mineralogical composition of ilmenite fines and titanium fume.

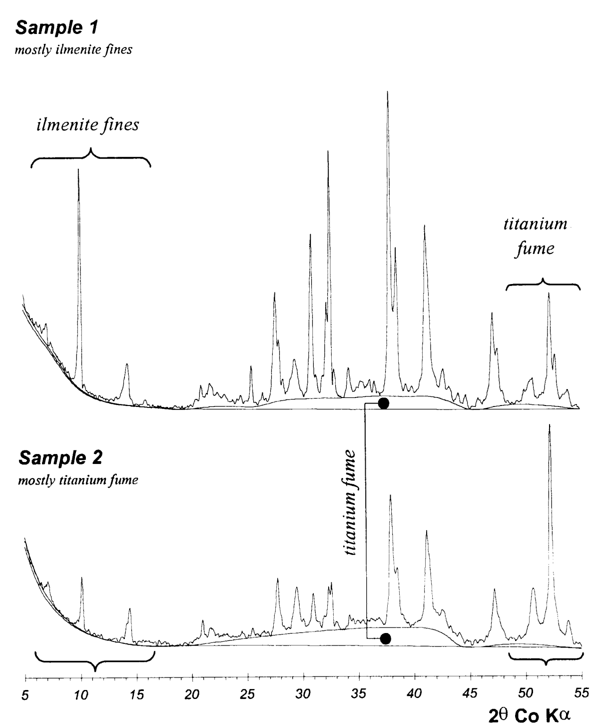

Fig. 5. XRD patterns of blended by-products.

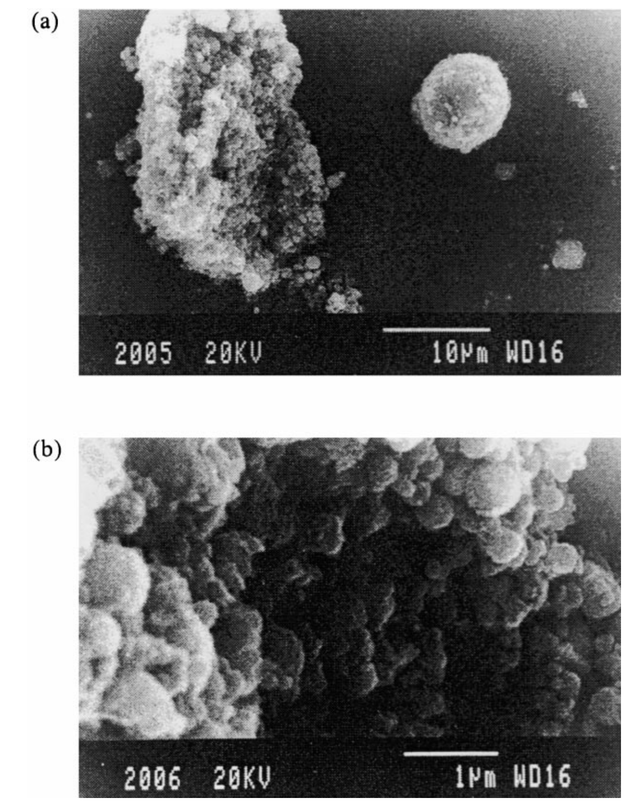

Fig. 6. (a) Agglomeration of elementary particles of titanium fume (SEM). (b) Detail of the agglomerates.

composed of metal iron and various titanium oxides. The quantitative analysis of the mineral and vitreous phases is difficult to obtain, due to the complexity of the material, and

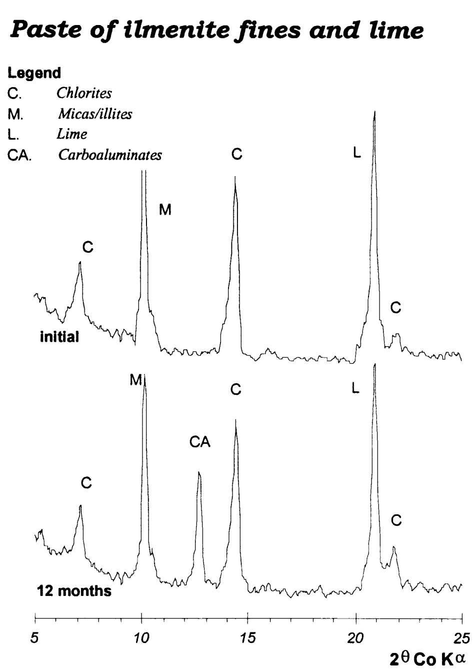

Fig. 7. Evolution of XRD patterns of an ilmenite fines/lime mixture as a function of time.

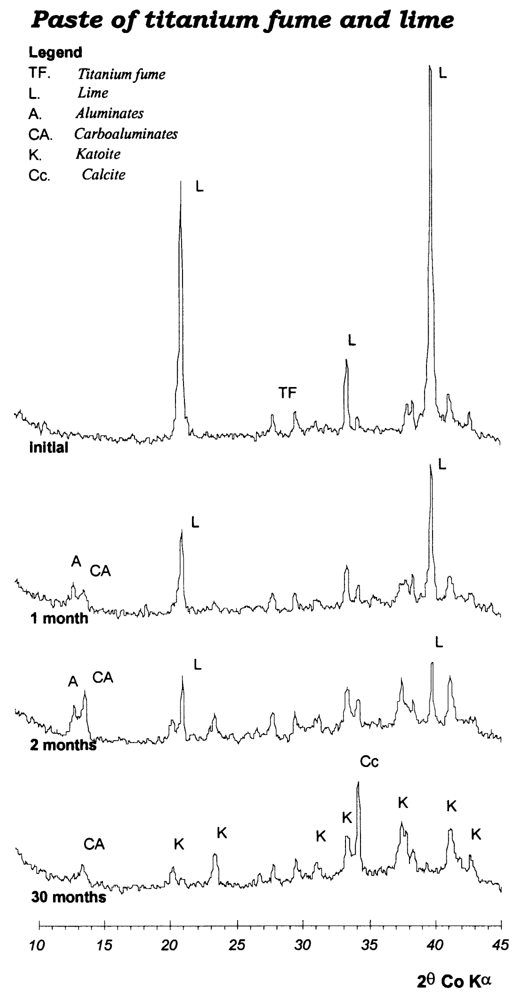

Fig. 8. Evolution of XRD patterns of a titanium fume/lime mixture as a function of time.

considering that it does not satisfy the basic requirements of a vitreous matrix of composition similar to that of crystalline minerals [1].

4. The by-products available: different mixtures in variable physical states

4.1. Availability of the by-products

The previous section of this paper dealt with the characterization of the pure forms of the two by-products. However, the pure forms of by-product are not easily available because they are generally mixed together in the settling tank, in variable and unknown proportions. Fig. 5 shows XRD patterns of two typical mixtures of the two by-products.

4.2. Physical states of the by-products

As explained previously, the by-products are generally collected after reduction of their water content to 15%. The

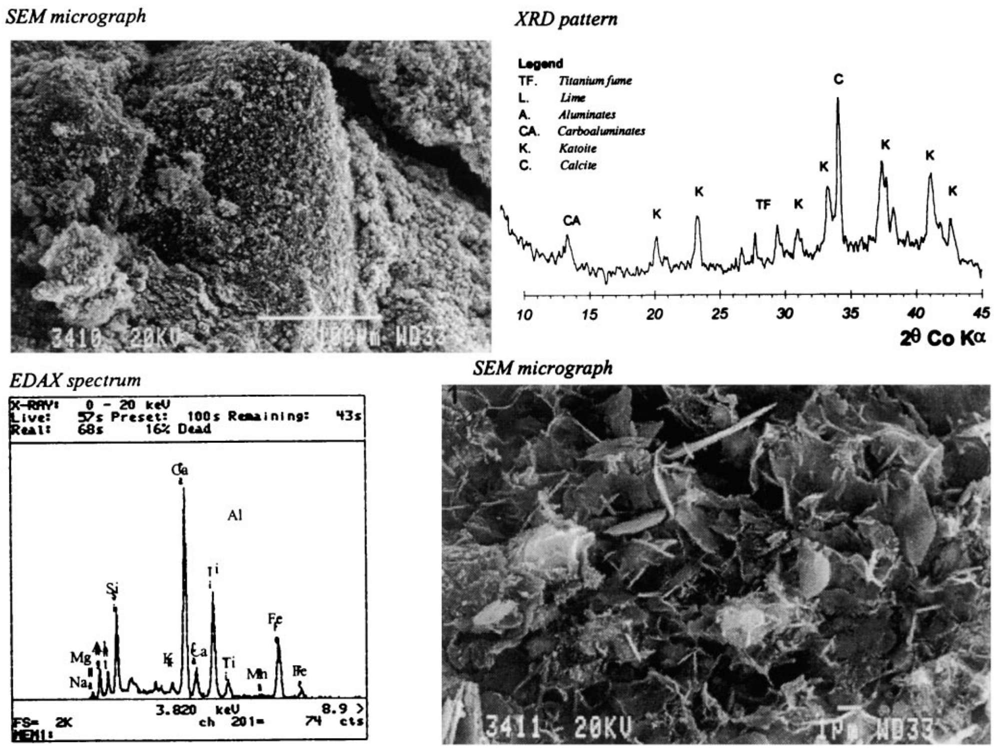

Fig. 9. SEM observation, EDAX and XRD spectra of some hydrates formed by the reaction of titanium fume with lime and water.

compactness of the cakes can, however, interfere with the use of these materials since the tight agglomerations of particles may be difficult to break (Fig. 6). This is a major problem for the improvement of the potential fineness of

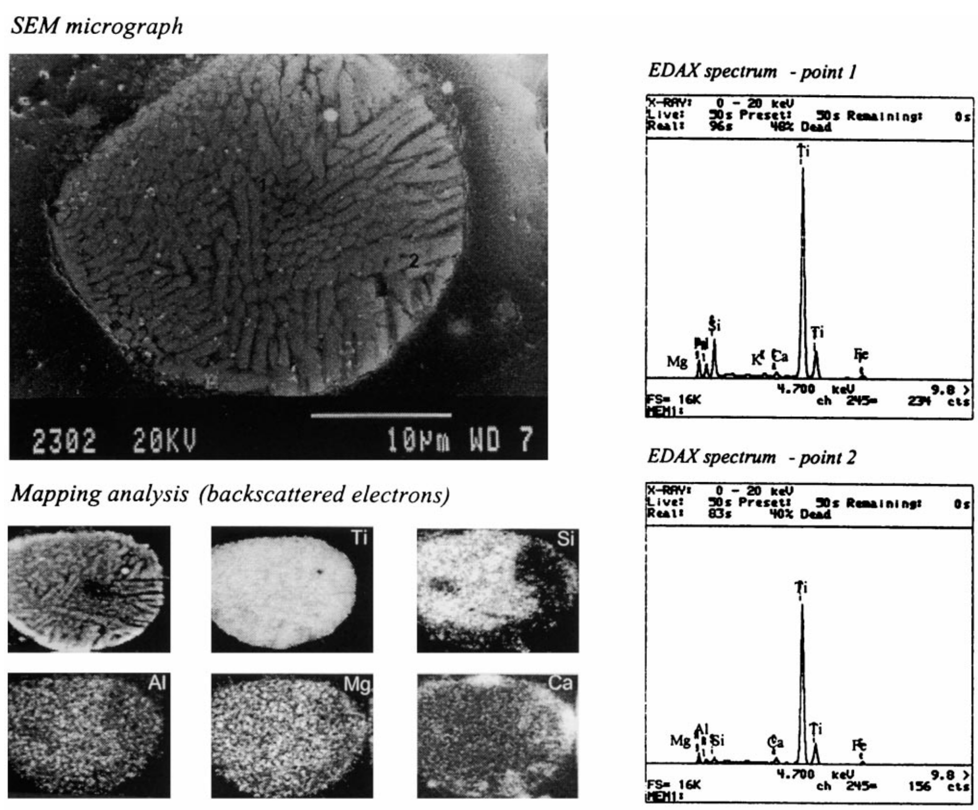

Fig. 10. Microscope analysis of a grain of titanium fume, after dissolution and reaction with lime.

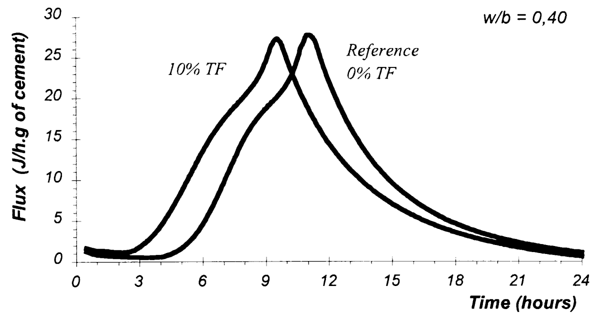

Fig. 11. Flux of hydration heat of cement pastes with and without titanium fume (TF), measured by adiabatic calorimetry.

these materials. To avoid the agglomeration of particles during the formation of cakes, it is possible to collect a slurry (solid content of approximately 50%) before its processing in the filter presses.

To take into account these industrial constraints (mix of by-products and their physical states), three samples of materials were examined.

Drycake1: a pure titanium fume obtained after drying and crushing the wet cakes for 2 h. SEM observations show that agglomerates of fine particles are still present.
Drycake2: a pure titanium fume obtained after 6 h of crushing. SEM observations show that most of the large agglomerates of more than 100 μm were broken.
Slurry: a slurry containing a mix of titanium fume and ilmenite fines. This is the most dispersed form of the by-products, since no drying was carried out on the materials.

5. Activity of the by-products

5.1. Reactivity in contact with water: hydraulic character of the by-products

Ilmenite fines and titanium fume do not appear to be hydraulic binders since no hardening occurs several months after mixing the by-products with water.

5.2. Reactivity in the presence of lime: pozzolanic activity of the by-products

The pozzolanic activity of ilmenite fines and titanium fume was evaluated by measuring the lime fixation capacity over time. Pastes of by-products, lime ($Ca(OH)_2$) and water (4:1:2, respectively, in mass) were made and the degree of reactivity was qualitatively assessed by observing the crystallographic changes (XRD) as a function of time.

These XRD patterns of the mixtures (Fig. 7) show that ilmenite fines are marginally reactive since only a small quantity of hydrates was detected and because lime consumption remains negligible. These hydrates, mostly calcium aluminates (C_4AH_x) and carboaluminates, were formed by the reaction of lime with chlorites and micas.

Titanium fume has a slightly higher reactivity than ilmenite fines but it remains relatively low compared to that of silica fume or fly ash. Fig. 8 illustrates the evolution of the XRD patterns of a titanium fume/lime mixture as a function of time. The patterns show an important lime consumption during first months. They reveal the presence of the same hydration products of the ilmenite fines and also the formation of hydrated calcium aluminates of the family of the katoites (C_3AH_6). SEM micrograph (Fig. 9) shows that some of the hydration products are in a compact mass of plates having a diameter of a few micrometers.

The analysis of a titanium fume particle, after dissolution and reaction, is shown in Fig. 10. The presence of grooves observed by SEM indicates that a part of the particle has been dissolved. One notes that previous observations, made on several titanium particles before their contact with lime and water, did not show these grooves. As shown by mapping analysis, the dissolution affected principally three elements: silicium, aluminium and magnesium. This is confirmed by EDAX analysis, showing a lack of these three elements as we progress from zones 1 to 2.

From a theoretical point of view, the titanium fume is a pozzolanic material, since its hydration consumes significant quantities of lime. However, this pozzolanicity leads to marginal technical benefits since even after 30 months, the paste remains friable and does not develop any significant mechanical properties.

5.3. Behavior in the presence of cement: activity of the by-products

The activity of titanium fume in cement pastes was analyzed by adiabatic calorimetry measurements [2].

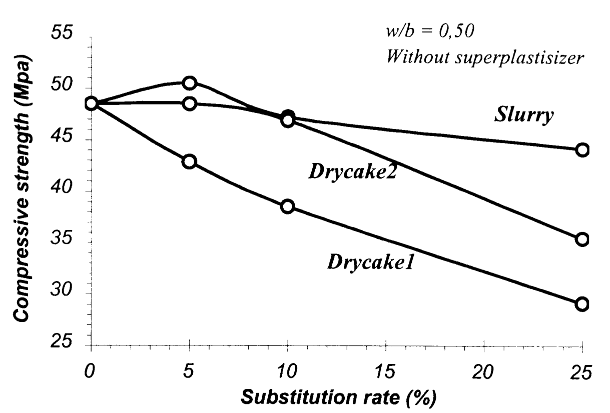

Fig. 12. Compressive strength of mortars at 28 days as a function of the cement substitution rate. Mix containing ilmenite fines and titanium fume (slurry and dried cakes). Each point on the curves is the mean value of six experimental results.

Table 2
French equivalence coefficient (k) for mineral admixtures [NF P 18-305]

Silica fume	1;2	Limestone	0.25	Slag	0.9
Fly ash	0.4;0.5;0.6	Quartz	0.10		

Fig. 11 shows the evolution of the flux of hydration heat of two cement pastes, with and without titanium fume. The curves show that titanium fume accelerates the kinetics of hydration by shortening the duration of the dormant period.

This phenomenon may be related to heterogeneous nucleation, where fine particles behave as germination sites for the hydrates, leading to the acceleration of the reactions.

6. The by-products in cementitious materials

It is well recognized that concrete strength (f_c) is directly proportional to binder strength (f_b). We choose to evaluate the benefits of using these by-products in concrete by measuring the strength of mixed binders made with these by-products. According to the European practice, this operation is generally carried out on mortars.

The mortars were made of one part of binder and three parts of sand (by mass) with a water to binder ratio (w/b) of 0.50 [NF EN 196-1]. A Portland cement, type CPA CEM I-42,5R [NF P 15-301] was used in all the mortars.

The replacement rates were 5%, 10% and 25% by mass. The 25% replacement is necessary in the evaluation of the activity index, in accordance with NF EN 450 standard. All the prismatic samples (4 × 4 × 16 cm) were stored in water up to the mechanical tests.

To take into account the various physical states, under which the by-products are recovered, we manufactured three series of mixtures from the by-products described earlier and named *Drycake1*, *Drycake2* and *Slurry.*

The results of the compression tests at 28 days, for each of the three series, are given on Fig. 12 (each point of the curves is the mean value of six experimental results). This figure shows the importance of the physical state of the by-products when used in cementitious materials. It can be noticed that materials with agglomerated particles (*Drycake1*) lead to significant loss of mechanical strength of mortars.

In our case, the use of 5% dispersed particles (*Drycake2* and *Slurry*) allows to obtain a strength equal to or higher than that of the reference without addition. Knowing (for these mixes) that the chemical reactions do not lead to an improvement of mechanical strength, we assume that the increase of strength is due to a physical effect, leading to the optimization of the granulometric curve of the mortars.

In order to quantify the effect of the by-products on the mechanical properties of the concretes, we use the concept of equivalent binder (B_{eq}) [NF P 18-305] [Eq. (1)]:

$$B_{eq} = C + kA \qquad (1)$$

where C and A are the masses of cement and addition used, and k is the efficiency coefficient of the addition. By definition, an addition with an identical behavior to that of cement, has a coefficient k equal to 1. The cement replacement can be done with equal weight, without lost of strength. The coefficient is 0 in the case of a chemically and physically inert addition: the material does not have any effect (positive or negative) on strength. A value of coefficient k lower than 0 means that the addition has a harmful effect on strength, its use decreasing the effectiveness of cement, while a value higher than 1 is equivalent to a higher activity, at the time considered, compared to that of cement. Lastly, a coefficient ranging between 0 and 1 indicates that the addition has an improving effect on strength, without however obtaining the effectiveness of cement.

For example, the French equivalence coefficient (k) of the principal mineral admixtures used in cementitious materials are listed in Table 2.

The calculation of coefficient k is carried out, for each mixture of each series, by using an adaptation of Bolomey formula [3] [Eq. (2)], giving the compressive strength f_c of mixture, in megapascals (MPa; the use of Abrams' law leads to similar results):

$$f_c = \alpha \left| \left[\frac{C + kA}{W} - 0.5 \right] \right. \qquad (2)$$

where α is a factor characterizing the cement and the granular skeleton, C, A and W are, respectively, the mass of cement, addition and water used. The coefficient α is calculated from the mixture containing no addition.

The calculation results of the efficiency coefficient k, relating to the various mixtures of the series, are illustrated in Fig. 13. The results show the following.

(a) The by-products have a significant activity only when their particles are dispersed (*Slurry*) or the large

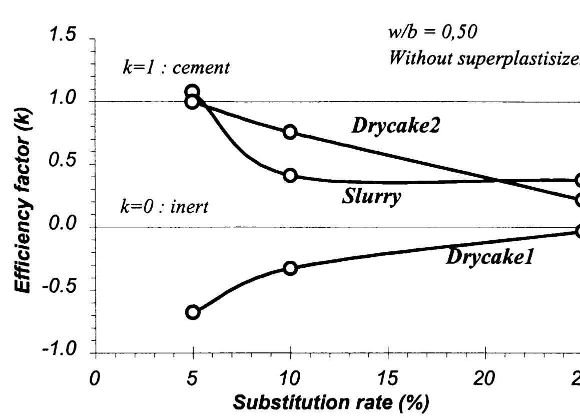

Fig. 13. Equivalence coefficient k of the by-products (B_{eq}=C+kA) calculated at 28 days by the Bolomey formula. Mix with ilmenite fine and titanium fume (dried cakes and slurry).

agglomerates are broken (*Drycake2*). This result is in agreement with the conclusions of Cyr et al. [4].
(b) The maximum activity is reached for small substitution rates, less than 10%.
(c) When 25% of titanium fume is used (in accordance with the activity index of the French standards), the efficiency factors are 0, 0.22 and 0.38, respectively, for *Drycake1*, *Drycake2* and *Slurry*. These results show that titanium fume can be compared to other inert fillers like limestone and quartz.

7. Conclusion

CA series of characterization experiments was conducted to evaluate two by-products from the iron and titanium industry (ilmenite fines and titanium fume) for their use in cement-based materials. The main conclusions are the following.

During the first month, these by-products show a weak reactivity with lime. Although after several months titanium fume consumes significant quantities of lime, this reactivity leads to marginal technical benefits since paste composed of titanium fume and lime remains friable and does not develop any significant mechanical properties.

The physical properties of these by-products, especially in the case of titanium fume, which is formed of spherical particles with a mean particle diameter of 1.7 μm, allow an enhancement of the mechanical strength of mortars, for mixed containing up to 5% replacement of cement. For larger substitution rates, their efficiency coefficient is between those of inert and pozzolanic materials.

Theoretically, it would be interesting to use the two by-products separately, titanium fume having a higher potential than ilmenite fines when used in concrete. Moreover, as it is generally the case for others industrials wastes, the existence of industrial constraints leads to practical problems for the utilization of the material, since we have to deal with the mixture of two by-products having different properties and with their recovery mode (cakes, slurry), leading to different physical states of the particles (dispersed or agglomerated). Our results show that dispersed materials allow higher mechanical strength of mortars then agglomerated materials.

These experiments show that ilmenite fines and titanium fume can be used in cement-based materials and that under certain conditions, they can even lead to an enhancement of mechanical properties of mortars. Complementary studies will be done soon to confirm these results and to study the behavior of these by-products in concrete.

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