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Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
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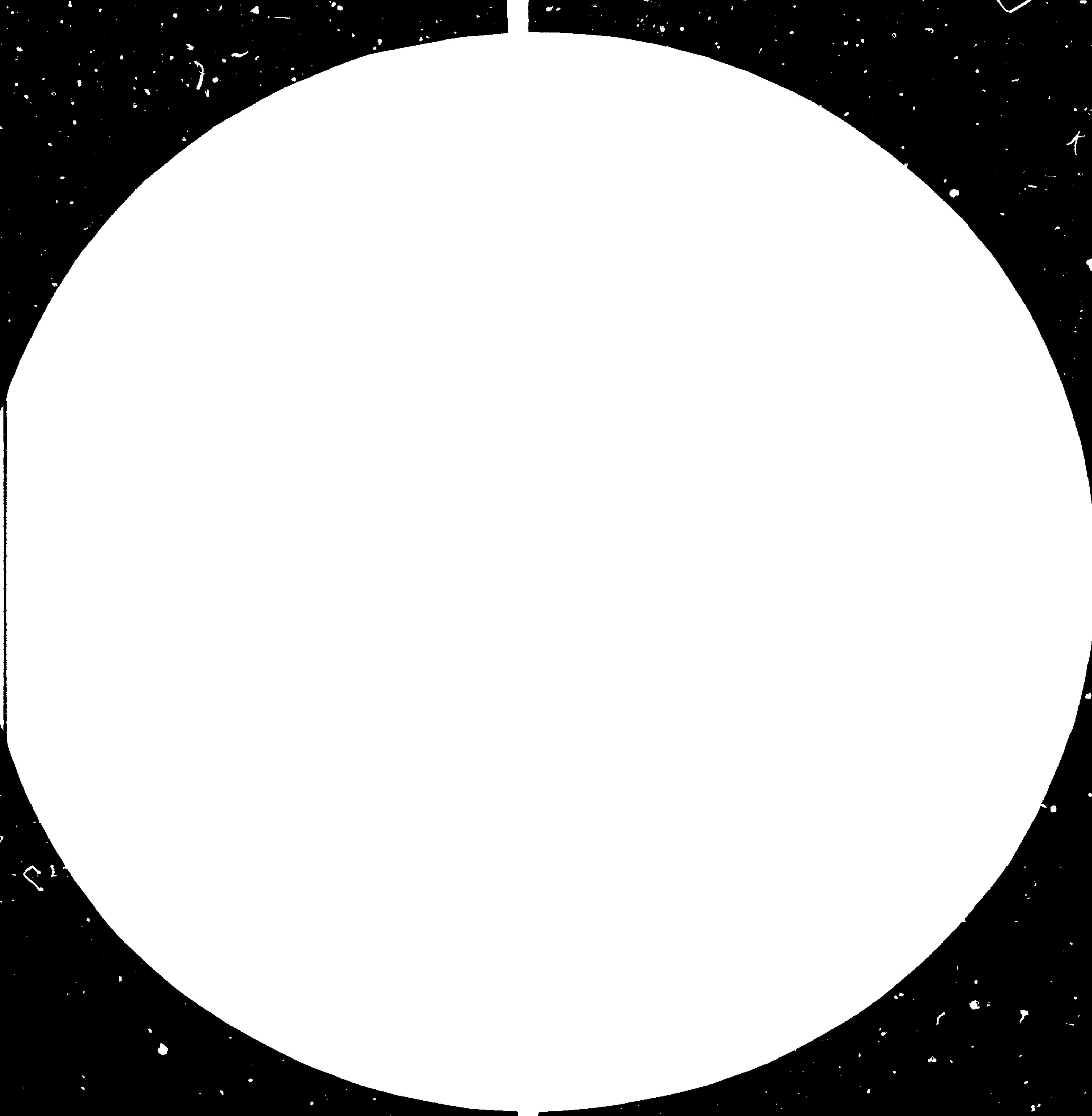

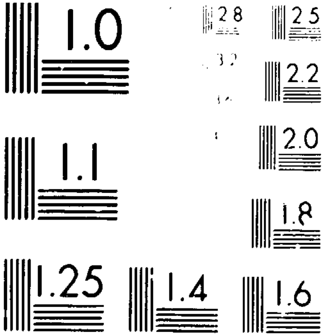
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HISTORY OF PFA USE IN FRANCE *

by

J. P. Meric **

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** Director General, Centre Technique Industriel, 23 rue de Cronstadt F75015 Paris, France

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SYNOPSIS

Fly ash is used in FRANCE in the manufacturing of various cement since 1952. There are some types of standard cements (for example CPJ) which can contain up to 35 % and some special binders made of a mixture of fly ash and slag.
This use does not correspond only to economic requirements but also to improve several properties of cement and concrete. Fly ash also finds many other outlets in road construction.

1 - INTRODUCTION

As in many industrial countries, the problem of using fly ash produced by dust removal from the fumes of thermal power stations heated with pulverized coal arose in FRANCE after world war II.

Shortly after, regulations became more severe regarding the purification of fumes in order to protect the environment and minimize pollution. A greater number of more efficient dust cleaners were placed in all thermal power stations. This meant that waste discharge rapidly caused many transportation, storage and even sometimes disposal and fixation problems.

Before 1952, pratically every fly ash was unused. It was put into heaps to form unaesthetic tips. The search for their use therefore became in FRANCE a national task and an economic imperative. Thanks to the perspicacity, the tenacity and the innovative spirit of some research workers such as P.M. FOUILLOUX and A. JARRIGE, outlets were rapidly found for ash, especially in the cement and concrete field where it can be fixed to modify favorably some properties. These properties became better understood thanks to studies carried out by the cement industry and C.E.R.I.L.H., as early as 1952, in cooperation with and thanks to the financial aid of two interested producers, C.E.R.CHAR and E.D.F..

In regard to the use of fly ash in cement works, C.E.R.I.L.H., in FRANCE, is the vanguard of progress and its studies have long been repaid by a hundredfold.

Nowadays, french cement plants use about 1 million tons of fly ash, that is about one fifth of the production. Since 1955, about 20 millions of tons of fly ash have been incorporated into cement. It is easy to evaluate the energy gain represented by this incorporation on the national level.

2 - FLY ASH IN FRANCE

In FRANCE, there are 19 stations belonging to "CHARBONNAGES de FRANCE" (french coal board) and 17 other stations belonging to "ELECTRICITE de FRANCE". Most of them are located in the North and in the Paris Region whereas the West has very few.

Table 1 gives the fly ash production in FRANCE since 1959 for CHARBONNAGES de FRANCE and ELECTRICITE de FRANCE (E.D.F.) stations and their uses in building and engineering industry.

Table 1

Years	Production in thousands of tons			Use in thousands of tons			Percentage of use
	C.D.F.	E.D.F.	Total	C.D.F.	E.D.F.	Total	
1959	1 989	664	2 653	355	160	515	19,4
1960	2 102	758	2 860	383	181	534	18,7
1965	2 704	1 318	4 022	1 146	978	2 124	52,8
1970	2 190	1 611	3 801	1 735	1 576	3 361	62,1
1971	2 874	1 687	4 561	1 953	884	2 837	62,2
1972	2 284	1 446	3 730	2 067	680	2 447	73,6
1973	2 651	964	3 615	2 0[illegible]4	473	2 567	71
1974	2 613	902	3 515	1 727	693	2 420	68,8
1975	2 106	1 242	3 348	1 645	713	2 358	70,4
1976	3 162	1 869	5 031	1 628	912	2 540	50,5

(after P. MARIE - E.D.F.)

Starting from 1976, a growing fly ash production can be noted, that will continue in the coming years. In fact, owing to the enhancement of fuel prices some thermal power stations will use pulverized coal instead of fuel. Thus, 5 millions of tons of fly ash were obtained in 1976 from 22 millions of tons of coal.

They are to be distinguished :

a) Siliceous-aluminous coal-fly ash essentially composed of silica, alumina, iron oxide and a little lime. Their grading stretches from a few micrometers to 200 micrometers, that is their Blaine surface area extends from 2 500 to 4 000 cm2/g (a fineness comparable to that of an ordinary cement). Fig. 1 gives the upper and under grain distribution curves and Table 2 gives the mean chemical composition.

Table 2

Chemical composition of scme fly ash (carbon deduced) in FRANCE

Elements %	coal-fly-ash (Nord - Pas-de-Calais)	lignite-ash	
		GARDANNE (Bouches-du-Rhône)	ARJUZANX (Landes)
SiO_2	52	30	35
Al_2O_3	30	8	12
Fe_2O_3	8	6	33
CaO	3	44	10
MgO	2	2	2
K_2O	3,5	) 4	) 1
Na_2O	1	)	)
SO_3	0,5	6	7

The amount of unburnt for all fly ash varies from 1 to 6 %, but the variation for the same well regulated plant is very low ($\pm$ 0,5 %). This kind of fly ash represents the biggest part of fly ash collected in FRANCE (95 %). Typical features of this fly ash are given in Table 3.

Table 3

Principal features of siliceous-aluminous coal-fly ash

Features			Values
Fineness	grading (µm)		0,5 à 200
	Blaine fineness (cm2/g)		2 500 à 4 000
	BET fineness (cm2/g)		8 000 à 15 000
Apparent density (kg/dm3)	dry	loose	0,55 à 0,80
		pressed	0,75 à 0,90
	wet		0,95 à 1,20
Specific gravity (kg/dm3)	raw		1,9 à 2,2
	after milling		2,6
melting temperature (°C)			1 230 - 1 450
amount of unburnt (%)			1 à 6
ignition loss (%)			2
insoluble (AFNOR) (%)			80 à 90

Fig. 2 shows the appearance of this kind of fly-ash.

b) melted siliceous-aluminous fly-ash produced by two stations. This fly ash is in a liquid state because of the high combustion heat and the relatively low melting point. Melted fly ash is granulated by water quenching in the same manner as for the granulation of blast furnace slag. It occurs then in the form of balls with 1 to 3 mm diameter which are easy to stock and contain pratically no unburnt. It has about the same chemical composition as the former fly ash.

c) lignite fly-ash also produced by two stations. It has very different properties and chemical composition (Table 2). It contains much more lime which must be perfectly extinguished in order to ovoid later expansion of concrete to which it can be added (especially in regard to the GARDANNE fly ash). It is a true binder called hydraulic ash.

Fly ash is collected into large storage and homogeneising beds or occasionally into bins. It is delivered to the different users either in a dry or in a wet state:

- in a dry state with the help of tank-waggons (railway), barges (waterway), but more commonly by air pressure Lorry (by road). Covered trucks may be used for small amounts, ~~the upper~~ layer being slightly humidified.

- in a wet state with the help of special waggons or trucks. It then contains 6 to 12 % of water. It can receive in exceptional cases up to 30 % of water and be removed in pipes as liquids in order to supply a cement plant working by the wet process and located near a thermal power station.

3 - USE OF FLY ASH IN THE CEMENT INDUSTRY

a) History

The idea of incorporating fly ash to cement dates back to 1951 when P. FOUILLOUX took out a patent (n° 1035771 delivered on April 5th, 1951). He recommanded not only the addition of fly ash to clinker and gypsum but supplementarily the addition of blast furnace slag. This approach of adding fly ash to cement was a consistent way of thinking, since Romans had long used lime and volcanic ash mixtures, the chemical composition of which was approaching that of thermal power fly ash. P. FOUILLOUX had the merit of having communicated his ideas, convinced people and commercialised very quickly, in 1951, cements made of ash, slag, clinker and gypsum (so called pouzzolano-metallurgical cements). The production of this kind of cement was 25 000 tons in 1952, 200 000 tons in 1962 and 500 000 tons in 1966 (that is 15 years after the patent deposit). In April 1959, AFNOR (the french standardization institute) standardized CPAC (containing from 5 to 20 % of fly ash) and CPALC (containing from 5 to 20 % of fly ash and slag). These cements have been used in FRANCE since then.

b) Utilization as raw material

Fly ash can be used as a raw material in cement production in place of clay, as it brings the necessary silica, alumina and iron. The unburnt that remains in it constitutes a non negligible fuel supply. It has once been used in a wet state in the wet process but is mostly used presently in a dry state in the dry process. It offers many advantages for the cement producer for it eliminates the grinding and drying of clay and thus, several cement plants have abandoned the exploitation of their clay quarry.

c) Utilization for the production of different hydraulic binders

Most of the time, fly ash is used as a component of hydraulic binders and added during the grinding. Besides, grinding is improved because fly ash acts somewhat as a grinding agent. Output increases of about 5 to 10 % were observed for industrial mills when replacing ordinary cement (CPA) by a cement containing 15 % of fly ash.

The current french standards (P 15-301) allow the addition of fly ash to CPJ (combined portland cement). This kind of cement can contain up to 35 % of fly ash or slag or pozzolan or filler (or mixtures of these materials). Thus, standardized cements containing up to 35 % of ash can be produced.

The corresponding compressive strength classes at 28 days are the following : 35, 45, 45 R, 55 and 55 R (R for rapid cement with a strength test at 2 days).

The other binders that could contain some fly ash are slag and pozzolan cements. The best known and the oldest are CPMF n° 1 (minimum strength at 7 and 28 days of 160 and 300 daN/cm2 respectively), CPMF n° 2 (minimum strength at 7 and 28 days of 210 and 375 daN/cm2 respectively). They contain 50 to 70 % of a slag and fly ash mixture. They are controlled by the Laboratoire de la VILLE de PARIS (VP Label) and figure on the list of cements allowed for marine construction.

Other binders can also contain ash : masonry binders, artificial hydraulic limes, special binders for the production of soil-cement in road technologies.

d) Properties of cements containing fly ash

Fly ash cements give more plastic mortars and concretes and with less bleeding. The setting times may be somewhat increased especially in cold weather. In order to accelerate the setting, one can add from about 0,5 to 1 % of sodium aluminate to a cement containing 30 % of fly ash. Mechanical strengths at 7 days and later are increased due to the pozzolanic effect of ash. Thus, similar strengths for cement with and without ash can be obtained :

- at the age of 28 days with 10 % of ash
- at the age of 6 months with 15 % of ash
- at the age of 3 years with 30 % of ash.

Fig. 3 shows plainly the pozzolanic effect of a quality ash. This effect is due to the fixation by silica and alumina of fly ash of certain excess of clinker bases during the hydration, especially of lime and alcalis. The determination of the ashes (or other material's) pozzolanic effect has given rise to numerous research studies based on physical, chemical or mechanical considerations. For this purpose, French often use the FERET law. Hydration heats are reduced during the first few days. Therefore the ash cements are used for mass works where thermal shrinkage is to be feared and may cause structural cracking (VOUGLANS dam, in FRANCE, was built with a portland cement containing 20 % of melted ash).

Cements with fly ash are particularly suitable for heat curing due to the acceleration of the pozzolanic effect.

Hydraulic shrinkage after setting is often reduced more or less by the addition of fly ash to cement. This can be partially explained by the fact that cement always contains a little amount of soluble alcalis (from 0,1 to 0,3 % of $Na_2O + K_2O$), that increase the shrinkage. Ash slowly combines with these alcalis to form stable and insoluble silicoaluminates. Moreover, this ability to absorb and insolubilize alcalis has been used in some countries where reactive siliceous aggregates are to be found, that may cause expansion due to alcalis attack.

It is observed that the utilization of ash cement improves the concrete stability to aggressive waters action in complete immersion. This improvement can be attributed to :
- reduction of the total amount of tricalcium aluminate (principal chemical responsable for corrosion by sulphated waters),
- smaller amount of hydrated lime $Ca(OH)_2$,
- increased fineness,
- increased absolute binder volume,

(the optimum amount of ash to resist aggressive agents would be from about 30 %).

Ash also acts as a stabilizer of eventual expansive agents (gypsum, free lime and magnesia).

In addition to these advantages come furthermore :
- lightening of precast structures,
- improved fire (due to the fixation of $Ca(OH)_2$) and thermal shock stability,
- reduction of binder cost (especially when the cement plant is located near a thermal power station).

4 - OTHER UTILIZATIONS

a) Utilization in concrete

Due to its fineness, shape, superficial state and low density ash improves mortar and concrete workability. The improvement is more marked for a finer ash (in an ash cement, ash has a fineness of about 5 000 cm2/g). There exists, for each case, an optimum ash percentage giving the best workability : for example, 30 % of ash. Moreever, the optimum can be easily determined.

With the addition of ash, it is possible :

- to reduce the mixing water quantity to obtain the same workability,
- to increase the concrete homogeneity and compacity and to improve its placing,
- to obtain a better shape after demolding.

With the addition of ash to concrete (in the amount of 30 to 100 kg of ash per m3 of concrete) it is possible to complete the grading and eventually correct sand lacking fines particules. It can even replace a part of the sand (for example 20 to 30 %). Therefore, this addition is particularly interesting at working sites for rather lean, low cement-rated, dry concrete mixtures.

Ash is used:

- in ready mix concrete plants,
- in precast-concrete plants, for the production of blocks, pipes, chimney-flues,
- in certain permanent structures (coolers, thermal stations' chimneys)
- for the production of lightweight autoclaved concrete.

b) Utilization for roads construction

Ash has been used very often for road technique since 1963. Furnace ash and wet fly ash are used for embankments stabilization and certain soils treatment. Ash allows the constitution of anti-contamination and filtration layers impeding an eventual clay rising. This ash can be easily compacted.

Dry fly ash is also used for the production of form layers, foundations and base layers in new road techniques.

An amount of 15 % of a fly ash, lime and gypsum mixture is added to the gravel . The mixture might have, for example, following composition : ash 90 %, lime 5 %, gypsum 5 %. A number of road constructions have been made, especially in the North, according to this technique which represents a real interest from an economic (when constructions are located near thermal power stations) and technical point of view because the material can be placed and correctly compacted before setting that is rather slow.

In conclusion, let us remember the words of Louis ARMAND of the "ACADEMIE FRANÇAISE" on the use of fly ash :
"To make from these pollutants useful elements is one of the finest results of regeneration for which this technique can be justifiably proud".

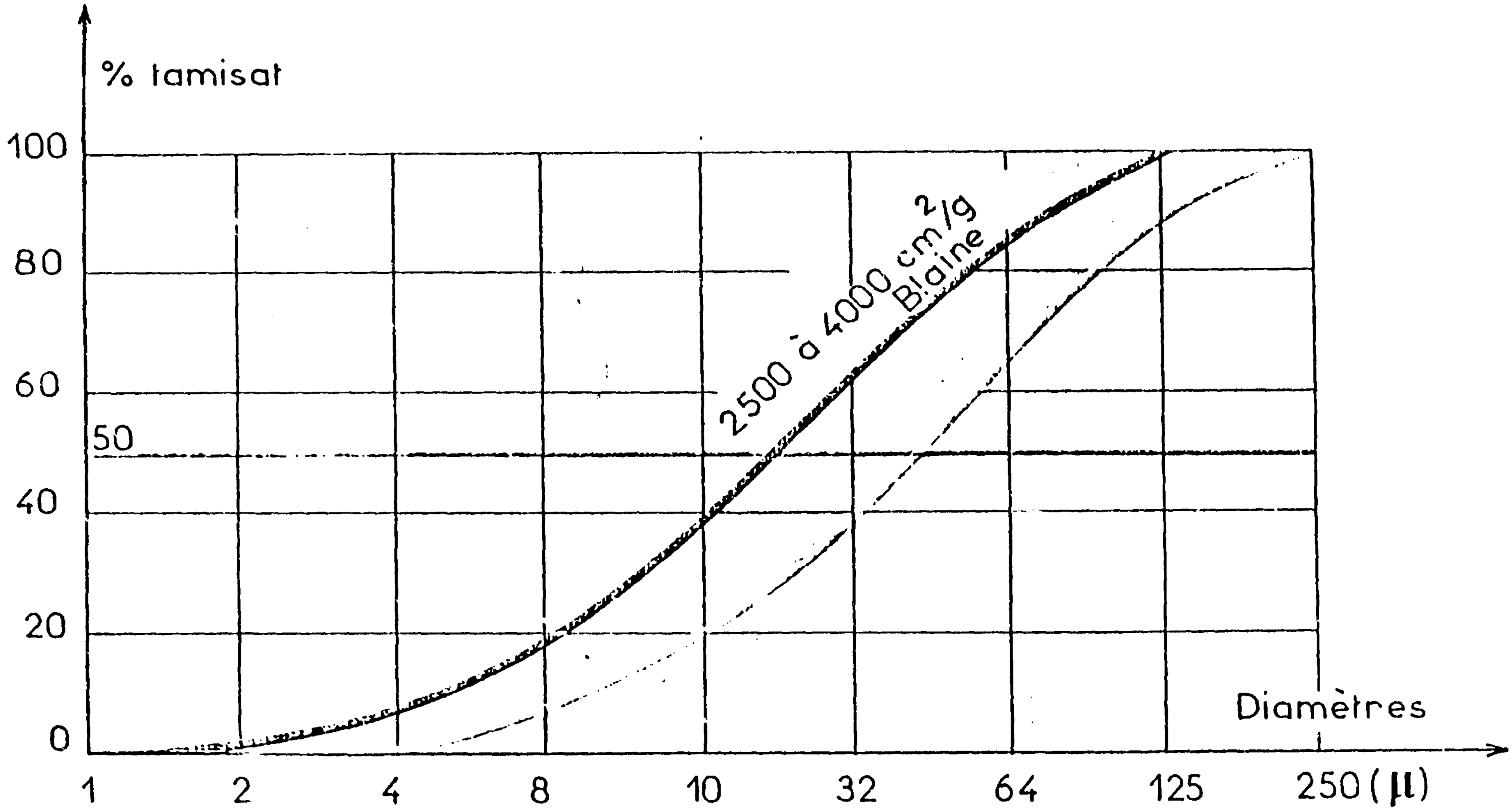

Fig. 1 Fuseau granulométrique contenant les cendres volantes utilisées en cimenterie _ (en France)

Figure No.2

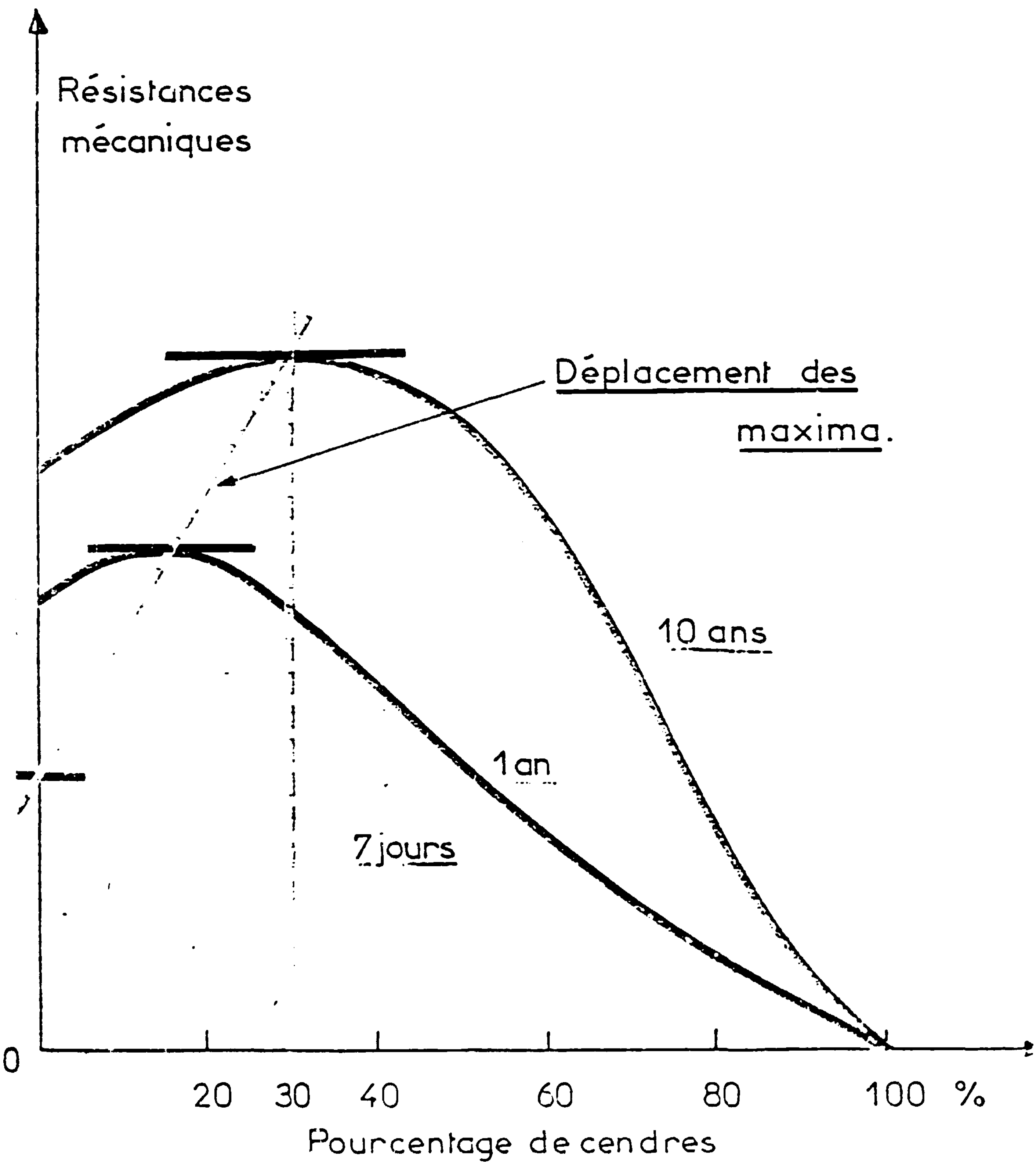

Fig. 3 _ Schéma de l'activé pouzzolanique des cendre volantes _