

Low Cost Grinding Aids for Cement

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Due to the current economic crisis and the situation in progress in the construction industry, Spanish cement producers have been obliged to take several measures in order to notably reduce costs.

In light of this situation, Proquicesa decided to focus its R&D efforts on the development of an innovative family of grinding aids, adapted to the new requirements of cement producers. In this way, Proquicesa has maintained its commitment to offering adequate technical solutions to customers' needs.

Thus, the company started an overall research project with the aim of finding new chemical compounds that allowed it to reduce the economic significance of these kind of additives within total cement production costs. Finally, at the end of 2008, Proquicesa introduced a new family of grinding aids with an excellent cost/benefit ratio, called ADITOR® M, which are formulated as an optimal combination of some alternative raw materials.

Today, the ADITOR® M are already being employed in several cement plants in Spain, and they are also being tested at industrial scale in some other plants, generating excellent results with respect to their technical performance and the economic savings obtained for the cement producers.

In this article, the most significant data and conclusions obtained from this research project are shown, as well as some of the most significant results achieved in its industrial application.

Introduction

In the current worldwide economic situation, the construction sector has been one of the most deeply affected. In particular, cement production in Spain decreased by 23% in 2008 relative to 2007.¹ Due to this huge drop and the forecast for the coming years, cement producers feel obliged to take measures to drastically reduce production costs.

One of the fields most affected by these cost-reducing measures is the grinding aids sector, which has been

gradually suffering a decrease in demand and changes in its field of application. These types of chemical admixtures, which were employed as specific products with high technical performance (i.e. quality improvers), are now in demand as plain surfactants for the grinding process, under targets based on a minimum price and dosage.

Grinding aids have been traditionally used to improve the efficiency of the cement moltruration process, one

of the most energy consuming processes in cement production (60 - 70% of the total electricity consumed in a cement plant). Grinding aids are normally liquid products, traditionally formulated as water-based solutions of organic compounds with high charge density, such as glycols, esters of glycols, alkanolamines and/or carboxylates of alkanolamines.² They are usually added at the entrance of the mill together with fresh feed,

composed of clinker and mineral admixtures.

The main function of grinding aids is to partially neutralise the charges present on the surface of cement particles, which develop during milling, reducing the surface free energy of the material being ground. For this purpose, the additive molecules are adsorbed over the surface of the cement particles by weak electrostatic forces, favouring the repulsion and/or a steric hindrance

between particles, avoiding their agglomeration and thus improving grinding efficiency. Similarly, the 'coating' effect is partially or totally avoided, enhancing other issues such as handling and storage conditions (boosting the 'pack set') or the

separator efficiency.³

Recently, the effect of grinding aids has been studied extensively. Many chemical species have been evaluated (amines, glycols, phenols, etc.), employing different parameters in the characterisation of the performance of these products.⁴⁻⁸ The evaluation of the grinding aid performance of the additives is normally carried out by monitoring the evolution of fineness with the operation time.⁹⁻¹⁵ From the technical literature, it can be concluded that the more representative parameters are:

- Breakage rate (C)^{16, 17}, defined as the slope of the evolution of fineness with time.
- Grindability index (GI), defined as the ratio between the fineness (determined by Blaine test) and the number of mill revolutions required to achieve that fineness.³

Proquicesa focused a great part of its R&D efforts on the development of a new family of additives, which is able to satisfy the current needs of cement producers, reducing its impact on production costs. This work led to the design and development of ADITOR® M, an innovative grinding aid based on an optimum combination of raw materials, some of which are obtained from byproducts of other industrial processes, providing an excellent cost:benefit ratio.

Some of the results obtained with this new product at both pilot plant and industrial scale are shown in this article. Moreover, the benefits achieved when using

Table 1. Chemical composition of CK (% wt.)										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	SC	Mineral phases*			
							C ₃ S	C ₂ S	C ₃ A	C ₄ AF
20.7	5.4	3.2	64.6	1.7	0.8	97.1	57.7	16.0	8.8	9.9

*By Bogue calculation

Table 2. Pilot plant grinding conditions		
Parameter	Value	
Mill	Speed (rpm)	55
	Temperature (°C)	~ 90
Grinding media (balls)	Diameter (mm)	15 - 32
	Ball-filling volume fraction (%)	~ 5
	Balls/material ratio (w/w)	9
	Mass (kg)	36
Material (CK+Gyp+grinding aid)	Mass of CK + Gyp (kg)	4
	Ultrafine CK addition (kg)	0.38
	Grinding aid dosage (ppm)	1000
Grinding process	Grinding time (min)	60
	Sampling time (min)	15



Figure 1. View of Proquicesa's pilot plant mills.



Figure 2. Fineness dry sieve test.

ADITOR® M compared to a traditional grinding aid (composed of amines and glycols) are established.

In this article, a technical viability and quality control analysis are also presented, paying special attention to the stability, manipulation and storage conditions of these additives, a key issue to consider when evaluating the industrial application of ADITOR® M.

Stages in the ADITOR® M development project

The work was structured in three main stages:

Pilot plant scale trials: verification stage

This involved the study of the performance of the new additives, as a grinding aid in a pilot plant cement molturnation process, in comparison with a traditional additive.

- Preliminary study to determine the most appropriate conditions for pilot plant milling, in order to obtain objective and significant results.
- Determination and evaluation of the grinding aid performance of the new additives.

Technical viability and quality control analysis

A study of the technical viability of the ADITOR® M formulation was carried out, in relation to its storage, manipulation, transport and chemical stability; as well as the establishment of proper quality parameters for these new additives, which include byproducts from other industrial processes as raw materials.

Industrial tests: validation stage

The performance of industrial trials in customers' facilities were evaluated in order to confirm the results obtained at pilot plant scale, concerning both the industrial grinding efficiency and the quality of the cements.

ADITOR® M pilot plant scale trials: verification stage

Materials and experimental procedure

The experiments at pilot plant scale were carried out using pure Portland cements, type CEM I¹⁸, composed of clinker (95%) and gypsum (5%). The materials were



Figure 3. Compression strength test.

Table 3. Fineness of the prepared cements, with and without grinding aid

Grinding time (min)	R32 μm (% wt)			
	Blank	ADITOR M1	ADITOR M2	ADITOR STD
0	90.0	90.0	90.0	90.0
30	59.4	47.1	52.8	42.2
45	35.5	21.7	20.7	30.3
60	18.4	10.1	7.8	11.7

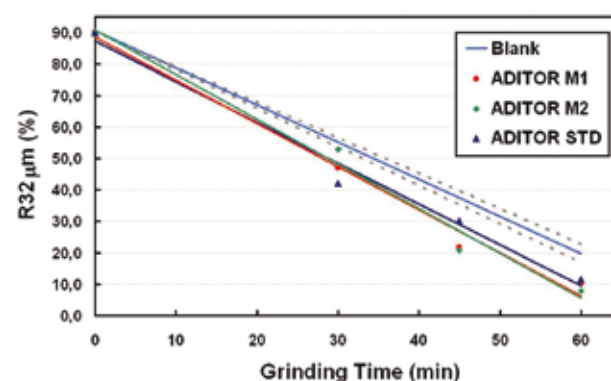


Figure 4. Fineness evolution of prepared cements, with and without grinding aid

Table 4. Values of C and GI of prepared cements, with and without grinding aid

Additive	C (%/min)	Blaine (cm^2/g)	GI ($\text{cm}^2/\text{g}\cdot\text{rev}$)
Blank	1.18 ± 0.05	3163	0.96 ± 0.04
ADITOR M1	1.37 ± 0.05	3493	1.06 ± 0.04
ADITOR M2	1.42 ± 0.05	3518	1.07 ± 0.04
ADITOR STD	1.29 ± 0.05	3336	1.01 ± 0.04

supplied by one of the most representative cement plants in Spain. The composition of the clinker is shown in Table 1.

In order to establish an objective comparison in the field of grinding aids, three additives were selected. Two of them, ADITOR M1 and ADITOR M2, are two formulations of the new family grinding aids; their chemical composition consists of a significant quantity of raw materials obtained as byproducts from other

Additive	Grinding time (min)	R32 μm (%)	Blaine (cm^2/g)	NC* (%wt)	IST** (min)	FST*** (min)
Blank	45	36.9	2331	28.0	230	270
	60	24.2	2816	28.0	205	265
	90	6.1	3770	29.0	185	225
	120	2.5	4447	30.0	170	240
ADITOR M1	30	47.1	1991	28.0	180	205
	45	21.7	2816	29.0	n/a	n/a
	60	10.1	3493	29.0	160	190
	90	3.2	4173	31.0	135	185
ADITOR M2	30	52.8	1840	28.4	205	255
	45	20.7	2916	30.0	170	210
	60	7.8	3518	31.0	155	195
	90	2.2	4226	31.8	150	195
ADITOR STD	30	42.2	2046	28.0	195	225
	45	30.3	2558	29.0	145	195
	60	11.7	3336	29.0	160	185
	90	3.1	4086	31.0	180	220

* Water to cement ratio for normal consistency
** Initial setting time, by Vicat needle method
*** Final setting time, by Vicat needle method

Additive	Grinding time (min)	Compressive strength (MPa)			
		1 day	2 days	7 days	28 days
Blank	45	6.4	11.4	29.6	40.5
	60	11.9	22.7	36.1	47.8
	90	19.8	30.5	41.9	55.0
	120	24.5	32.3	45.9	52.1
ADITOR M1	30	6.4	15.2	29.2	37.2
	45	13.9	23.8	35.9	47.7
	60	18.2	28.1	41.1	48.4
	90	20.8	32.0	43.1	52.6
ADITOR M2	30	5.1	11.8	23.0	31.2
	45	16.1	23.1	34.5	45.4
	60	21.2	30.0	40.9	51.0
	90	22.8	31.2	42.6	53.1
ADITOR STD	30	6.6	14.9	28.4	37.9
	45	12.3	20.4	33.4	37.9
	60	16.7	25.3	40.9	49.6
	90	19.8	31.3	40.5	47.4

industrial processes. The third, ADITOR STD, is one of the basic formulations of Proquicesa's traditional grinding aids: its composition is based on a combination of synthetic organic compounds derived from amines and glycols.

The experimental procedure for pilot plant scale trials has been described in detail in other publications.¹⁸⁻²⁰ Nevertheless, for this project, previous experiments were carried out in order to define the optimum operation conditions of the mills, and the grinding time required for a quantitative determination of the coadjutant properties

of the products. The procedure was then adapted and its experimental error was determined.¹⁸ Final operation conditions are shown in Table 2.

The test conditions allowed a similar practice to the industrial operation, and established the most appropriate variables for reliably determining the additive performance, maintaining a suitable efficiency in the moltration process carried out in pilot plant mills (Figure 1).

All the cements produced in the pilot plant were characterised according to the European Standards (EN). Moreover, the performance of cements produced with grinding aids was compared to those performed in the same conditions without additives (blanks), with the aim of determining the benefits of these additions (Figures 2 and 3).

Results and discussion

The more significant results obtained in the pilot plant study using ADITOR® M are shown in this article. These results were compared to those obtained from both the tests carried out without additives and the moltration performed with the ADITOR STD.

For cement fineness characterisation, the weight of residue on dry 32 μm sieve test (R32 μm) and Blaine surface⁹⁻¹⁵ were selected, as these parameters are the most representative in the study of cement fineness in the Spanish market. The following figures show the values of R32 μm (%) and Blaine (cm^2/g) obtained in the experiments performed with the studied additives. In this way, the improvements obtained by the addition of the grinding aids are clearly illustrated. The results of the mechanical and physical characterisation of the cements produced in Proquicesa's pilot plant employing grinding aids are also shown in the following Tables and Figures.

Grinding aids performance

With the aim of determining the grinding aid efficiency, two parameters were selected:

- Breakage rate (C, %/min), calculated from the slope of the linear regression of the evolution of R32 μm versus grinding time. (60 minutes of grinding, during which the efficiency of the moltration in the mills remains constant.)
- Grindability index (GI, $\text{cm}^2/\text{g}\cdot\text{rev}$), calculated as the ratio between the value of the Blaine surface after 60 minutes of grinding and the number of full rotations of the mill at that time.^{3,18}

The values of R32 μm obtained for prepared cements, with and without additives (blank, ADITOR M1, ADITOR M2 and ADITOR STD) are shown in Table 3 and Figure 4. Experimental error bars are also plotted as dashed lines in Figure 4. Table 4 shows the values of C and GI obtained from the tests performed with and without additives.

These results reveal that the new ADITOR® M offered slightly better grinding aid performance than

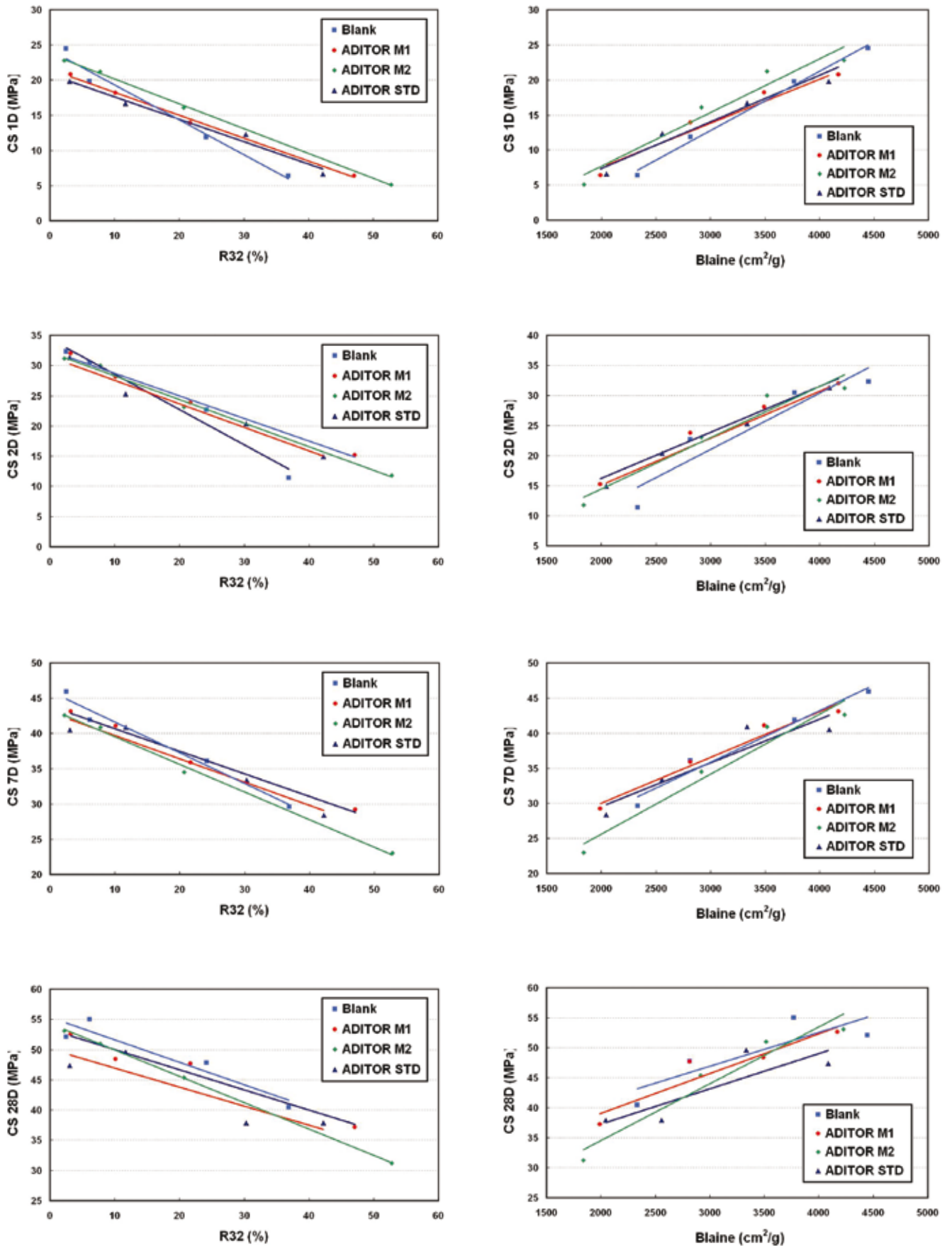


Figure 5. CS of the produced cement, with and without additive.

the ADITOR STD, showing breakage rates of 1.37 and 1.42 %/min, and values of GI of 1.06 and 1.07 cm²/g·rev for ADITOR M1 and ADITOR M2, respectively.

This performance is a clear indication of the high coadjutant power of this family of grinding aids, which can be converted to cost savings with respect to the industrial molturation conditions currently employed. ADITOR[®] M displayed a better performance than the traditional ADITOR STD formulation, but with a much lower cost, underlining the successful combination of

Additive	Relative additive cost	C:B ratio	
		(C:B) _C	(C:B) _{GI}
ADITOR M1	0.53	0.39	0.50
ADITOR M2	0.47	0.33	0.44
ADITOR STD	1.00	0.78	0.99

Table 8. Specifications and regulatory information of ADITOR M1, ADITOR M2 and ADITOR STD

	Parameter	ADITOR M1	ADITOR M2	ADITOR STD
	Physical aspect (at 20 °C)	Yellow liquid with slight characteristic smell	Brown liquid with slight characteristic smell	Colourless liquid with slight characteristic smell
Physical and chemicals properties	pH (at 20 ± 1 °C)	n.a.	n.a.	7.6 ± 1.0
	Density (at 20 ± 1 °C)	1.13 ± 0.03 g/cm ³	1.15 ± 0.03 g/cm ³	1.06 ± 0.03 g/cm ³
		< 0.5 ml/l	< 0.5 ml/l	< 0.5 ml/l
	Freezing point	-10 °C	< -20 °C	-5 °C
	Boiling point	104 °C	99 °C	98 °C
	Flash point	Non flammable	Non flammable	Non flammable
	Chloride content	Free (<0.1% w/w)	Free (<0.1% w/w)	Free (<0.1% w/w)
	Solubility in water	Fully miscible in all proportions	Fully miscible in all proportions	Fully miscible in all proportions
Handling and storage	Handling	Avoid contact with eyes, skin and clothes. Use PPE	No other requirements	Avoid contact with eyes, skin and clothes. Use PPE
	Suitable materials	Carbon steel, stainless steel, plastic materials	Carbon steel, stainless steel, plastic materials	Carbon steel, stainless steel, plastic materials. Avoid aluminium and cooper.
Regulatory information	Risk symbols	Xi - Irritant	Non-hazardous prepared under the applicable legislation	Xi - Irritant
	Risk phrases	R36, R37, R38		R36, R37, R38
	Safety phrases	S26, S36		S26, S36

species in the ADITOR[®] M formulation.

The effect of grinding aids

In order to determine the influence of grinding aid composition on the compressive strength (CS) reliably and independent of cement fineness, several grinding essays were carried out with varying grinding times (between 30 and 120 minutes), to produce cements with a fineness properly ranged to obtain results representative of the industrial processes (Blaine ~2000 - 4000 cm²/g, and R32 μm ~40.0 - 3.0%). At this point, four series of trials were performed: without additive, and with separate additions of 1000 ppm of ADITOR M1, ADITOR M2 and ADITOR STD.

The results from the mechanical and physical characterisation of the cements are shown in Tables 5 and 6, and Figure 5. The results in Figure 5 were adjusted to a linear regression to facilitate the comparison between the different series of experiments.

As expected, the higher the fineness of the cement, the higher the water:cement ratio for normal consistency for these experiments. On the other hand, the initial setting time decreased when the fineness increased, due to the acceleration in the hydration of the different phases composing the cement.

The results indicate that the influence of the grinding aids on the development of CS was minimal. Thus, the differences observed on CS results were included in the range of the experimental error defined for these trial conditions, in all the ages evaluated and for all the formulations tested.

Technical and economic advantages

In the last step of the pilot plant stage, an estimation of the potential economic profit of ADITOR[®] M was performed, compared to the traditional ADITOR STD formulation. For this purpose, the cost:benefit (C:B) ratio was defined as the ratio between the price of the product, in relative terms with respect to the ADITOR STD, and its performance as a grinding aid, quantitatively determined by C and GI. Thus, the ratios (C:B)_C and (C:B)_{GI} could be calculated.

These parameters can be a good indication of the potential economic savings by means of substituting the traditional formulations for ADITOR[®] M.

In Table 7, the ratios (C:B)_C and (C:B)_{IM} obtained for ADITOR M1, ADITOR M2 and ADITOR STD are shown.

It can be observed that the C:B ratios for the ADITOR M1 and the ADITOR M2 were drastically lower than the C:B ratio of ADITOR STD, due to the contribution of two main factors: the lower price (approximately 50% lower) and the slightly better performance of ADITOR[®] M. Thus, the values obtained for the potential benefits of using the new additives were up to 50% higher than using the traditional ones.

Conclusions

From the results of the research project carried out in Proquicesa's pilot plant for the development of ADITOR® M, the following conclusions can be underlined:

- The experimental procedure allowed the determination, in a proper and quantitative way, of the performance of the additives.
- ADITOR® M allowed the design of new grinding aids, improving upon the technical performance of the traditional ones.
- The addition of the new ADITOR® M to the cement grinding process did not significantly modify the physico-mechanical properties of the cements (such as setting time, CS or normal consistency water: cement ratio), in a similar way to the application of the traditional plain grinding aids.

Table 9. Statistical analysis of pH and density values of ADITOR M1, ADITOR M2 and ADITOR STD

Parameter	Density (20 °C) (g/cm ³)			pH (20 °C)		
	ADITOR M1	ADITOR M2	ADITOR STD	ADITOR M1	ADITOR M2	ADITOR STD
Average	1.154	1.124	1.061	8.09	7.93	7.57
Standard deviation (σ)	0.001	0.003	0.001	0.86	0.85	0.11
H.T.L. (3 σ)*	1.157	1.133	1.064	10.67	10.48	7.90
L.T.L. (3 σ)**	1.151	1.115	1.058	5.51	5.37	7.24

* H.T.L. (High Trust Limit) and L.T.L. (Low Trust Limit), calculated from the average ± standard deviation threefold. These parameters indicate the maximum deviation permitted by Proquicesa's Quality Management System for each industrial batch sample, and enable a decision on its storage and delivery. These are usually calculated one year after data collection.

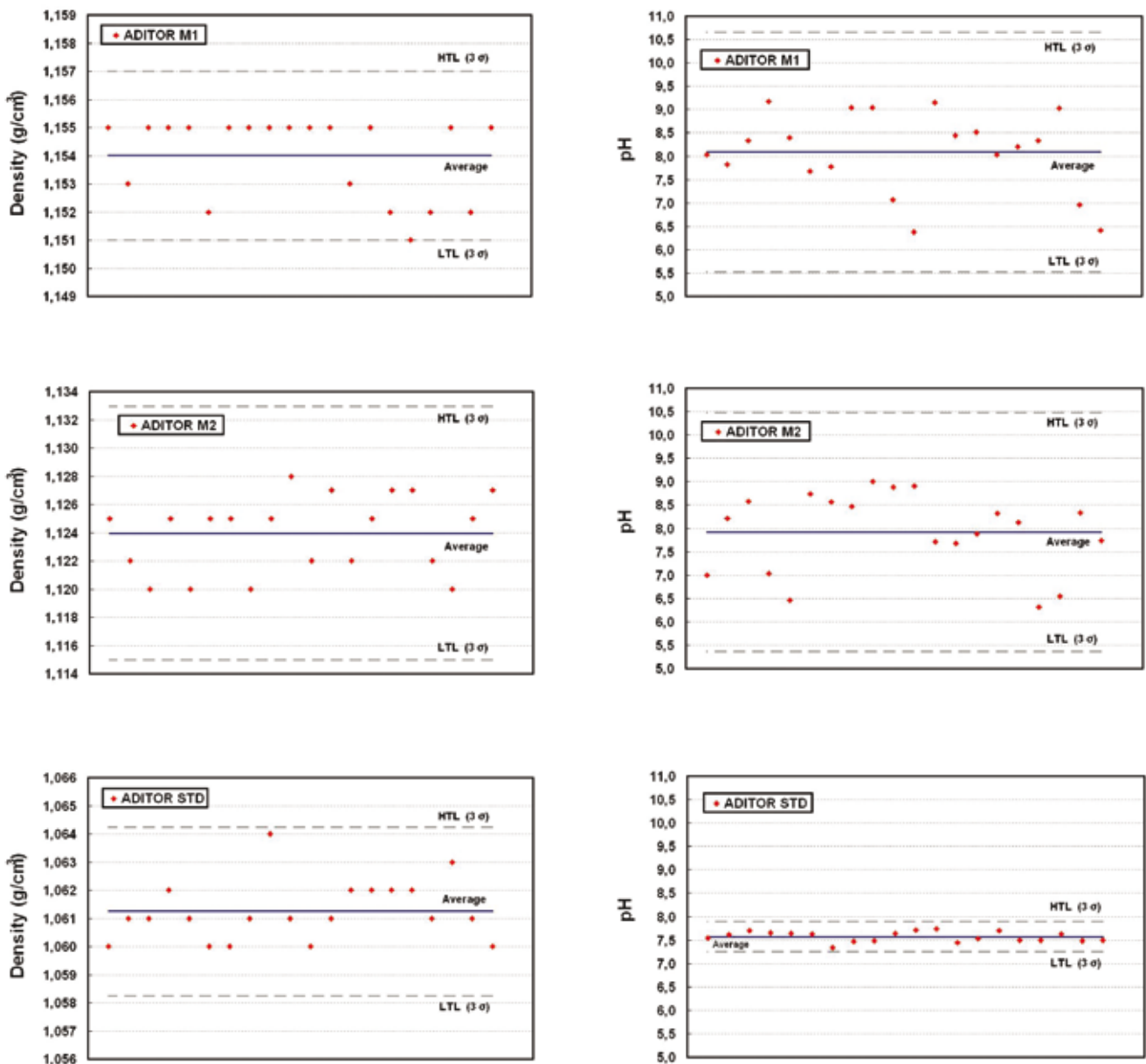


Figure 6. Density and pH values of ADITOR M1, ADITOR M2 and ADITOR STD, collected from the last 20 weeks industrial batches.

Table 10. Cost savings realised with ADITOR® M					
	Aid Ref.*	ADITOR® M			
Type of cement**	Dosage (g/Tm)	Dosage (g/Tm)	Rel. Price	Rel. Cost	Saving (%)
CEM I 52,5 R	800	300	0.67	0.25	75
CEM II/A-P 42,5 R	450	400	0.79	0.70	30
CEM II/B-P 32,5 N	350	350	0.65	0.65	35
CEM II/A-L 42,5 R	925	950	0.60	0.62	48
CEM II/B-L 32,5 N	900	925	0.58	0.60	40
BL I 52,5 R	350	350	0.53	0.53	47
I 42,5 R/SR	850	325	0.64	0.24	76

*The price of the regularly employed grinding aid and its cost were considered as a relative value of 1.00 in each case.
** UNE-EN 197-1

commonly and easily monitored by Spanish cement producers, as a direct and simple standard of stability and quality of the product. Thus, the additives' density and pH are the most frequently used quality standards in the cement industry.

The values of density and pH of the ADITOR M1, ADITOR M2 and

- The new ADITOR® M offered potential cost savings 50% higher than the traditional formulation.

Technical viability and quality control analysis

This stage of the project focused on the determination of the technical viability of the production and marketing of the ADITOR® M, under the strict controls of the quality management system ISO 9001, implemented from 2001.

For this reason, the physical-chemical properties normally used as technical specifications for grinding aids were determined, as well as the hazardous classification and the recommended handling and storage conditions. In the same way as before, these ADITOR® M features were compared to the properties of the traditional grinding aid.

Technical viability analysis: specifications and regulatory information

The study of the technical viability is a key issue in the case of the ADITOR® M, due to the employment of byproducts from other industrial processes as raw materials for its production. For this reason, a complete characterisation of the new ADITOR® M was required.

The main physical-chemical properties, regulatory information and handling and storage recommendations of the new additives are shown in Table 8. The information of ADITOR STD, as a reference of standard traditional coadjuvants, is also presented. From this information, it can be observed that the employment of subproducts of other industrial processes in the composition of the ADITOR® M did not have any significant effect on either the physical-chemical properties of the developed additive or the handling and storage recommendations.

Moreover, the employment of this type of byproduct allowed the formulation of additives that have no hazardous classification by the current Spanish law. This is an important advantage over the traditional additives, such as ADITOR STD, which are usually classified as irritant due to their composition.

Quality control: parameters and monitoring

Several physical-chemical properties are routinely analysed for each batch of grinding aid produced by Proquicesa as a requirement of the company's quality management system. Some of these parameters are

ADITOR STD, collected from the last 20 weeks, are shown in Figure 6. These values were obtained from the analysis of the batches produced at industrial scale. Table 9 presents the statistical analysis of these data.

From the statistical analysis, it can be observed that both ADITOR® M and ADITOR STD densities had similar reproducibilities (see the values of standard deviation in Table 9). However, the pH standard deviations of the ADITOR® M were greater than the deviation of the ADITOR STD. This can be due to the high amount of active matter (organic compounds) integrated in the composition of the ADITOR® M. In this way, the short quantity of free water incorporated in these formulations makes the pH an inaccuracy parameter. Thus, the variations on the pH are not representative of the product's composition stability.

Today, Proquicesa's Quality Department is working on the definition and development of new parameters and measuring techniques, which allow correct monitoring of the stability and quality of ADITOR® M. Furthermore, in order to guarantee the performance of the products in industrial applications, the Quality and R&D departments have developed a new validation protocol for the product, which not only monitored the physical-chemical properties of the additives produced industrially, but also intensifies and improves the quality control of the product, carrying out a periodic evaluation of the additive's performance in pilot grinding plant. Molturation tests are routinely carried out in pilot plant mills to determine the coadjuvant power of the additive and its effect on the quality of the cement.

Industrial tests: validation stage

For industrial implementation of these new grinding aids, some of the ADITOR® M formulations were offered for testing in various cement plants in Spain. Specific formulations were proposed in each case, depending on the different technical and/or economic situation of both the additive application and the type of cement produced.

In the first half of 2009, after eight months in the market, different ADITOR® M formulations have been validated in 14 Spanish cement plants, which equates to some 30% of the total cement production facilities in the country. The results have encouraged a high influx of the product into the Spanish market. At present, these products are being supplied to three of

the most important cement companies in the world, well-established in Spain, and also to other independent producers. Moreover, in the current market situation, the high technical performance obtained at industrial scale, and the significant savings offered, have caused cement producers to speed up the implementation process of these new grinding aids.

Table 10 shows the results obtained in some of the performed industrial essays. Those results were chosen taking into account the cement plants that already employ Proquicesa's products, with the aim of making a deeper discussion about the technical-economic advantages of the new additives. In this way, it was possible to deduce the cement production cost savings achieved by the substitution of the traditional grinding aids for the new ADITOR® M. Moreover, the more representative cement types in the Spanish market are evaluated (according to the EN).

As can be seen in Table 10, the cost saving caused by the aids' substitution was defined as the main parameter (saving). Furthermore, the dosage of ADITOR® M, and the price (rel. price) and cost (rel. cost) of the new aids referred to the traditional one (aid ref.), are also shown in Table 10.

In all the cases, the hourly production of the mills was maintained as a set point for the trials, in order to establish an objective comparison between tested additives.

On the other hand, the quality of the cements produced at industrial scale was not affected by the employment of the ADITOR® M.

The results obtained with ADITOR® M show that, by using the additives, up to 75% cost savings were obtained, confirming the estimation of the potential cost-benefit ratio calculated from the pilot plant scale results. This saving implies a significant reduction in cement production costs.


Conclusion

The analysis of the results obtained from this study demonstrates the technical and economic viability of the formulations developed for the new family of additives in the industrial cement grinding process.

From this work, the following conclusions can be obtained:

- The formulations developed for the new low cost grinding aids allowed the incorporation of chemical products from other industrial processes into the traditional composition of these aids. These new formulations modified neither the chemical stability or physical-chemical properties, nor their hazardous classification or handling and storage recommendations.
- The parameters and procedures followed for the quality control guarantee its composition stability and performance as a cement grinding aid.
- The industrial performance of ADITOR® M improved the results obtained by the traditional aids, highlighting the selection and combination of chemical products in its formulation.
- The industrial employment of ADITOR® M in the cement molturation process provided, for the tested

cements, up to 75% savings compared to traditional grinding aids, maintaining the mill efficiency, the cement production and the cement quality as constant.

In conclusion, the new ADITOR® M of Proquicesa has demonstrated to be an excellent technical and economic solution for the cement molturation, enabling a drastic reduction of the grinding cost whilst maintaining the cement quality, which is especially important in view of the current situation in the construction industry. 

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