USE OF CALCIUM OXIDE IN CLEANING BORATES IN CERAMIC FRIT MILLING EFFLUENTS

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ABSTRACT

Borates are widely used in the ceramic industry in glaze production, so that they are also found in the arising waste. The presence of boron in wastewater involves an environmental problem for citriculture in Castellón (Spain), given the sensitivity of orange trees to borates. Although sludges can be reused in the spray-drying stage, the addition of borates as fluxes to porcelain tile in glazed and polished glazed porcelain tile processes impedes using borate-containing sludges, in this case requiring the separation of borate from the waste. Amongst the agrochemical practices employed to palliate borate pollution, $Ca(NO_3)_2$ fertilisation is used as a result of the relative lower solubility of calcium borates, which remain fixed in the soil. The possibility was analysed in the present work of using this agrochemical criterion for cleaning wastewater from the ceramic tile industry, in which the main borate contribution to wastewater arises in glaze milling. The effect of precipitation with CaO and the addition of $Ca(NO_3)_2$ was therefore studied in the precipitation-decantation process of the wastewater from milling three types of ceramic frits, comparing the results with the usual precipitation-decantation process with NaOH.

1. INTRODUCTION

Borates are used as an important glaze-firing component in the ceramic floor and wall tile industry. The minerals used in fritting include: Borax $Na_2B_4O_5(OH)_4$, Colemanite $B_6O_{11}Ca_{2,5}.H_2O$, Kernite $B_4O_7Na_2.4H_2O$ and Boracite $B_{14}O_{16}Cl_2Mg_6$. Boric acid is also a widely used synthetic additive in ceramics. Borates appear furthermore as perborates ($Na_2B_2O_4(OH)_4$), as whiteners in commercial detergents on producing peroxides by hydrolysis.

Borate toxicity has been evaluated in tank facilities as Eldea canadiensis and Myriophillum alterniflorum (10 ppm) or in Ranunculus penicilatus (5 ppm). The FPV (Final Plant Value) is estimated at 5 ppm. The Final Chronic Value and Final Residue Value are not available in the literature, as contradictory values are found.

Boron is a widespread element in nature, with a presence of 0,1-15 ppm in surface waters and 4-5 ppm in the oceans. In the ground it ranges from 10-300 mg/kg [1]. Boron is citrotoxic. Orange trees cannot be continuously watered with water containing over 0,2 ppm boron, regulated by the Law on Waters [2] quality limit 10 ppm in Table 1 of the Regulations of the Hydraulic Public Dominion).

Although sludges can be reused in the spray-drying stage, the recent practice of adding borates as fluxes to porcelain tile bodies in glazed as well as polished glaze processes impedes this recycling practice with sludges, as the presence of rests of grinding elements and the addition of these sludges can alter body colour. It is therefore necessary in these cases to separate boron from the discharge by simple processes that do not generate high rates of borate concentrates in the cleaning processes, as is the case with ion-exchanging zeolites or inverse osmosis systems [3].

As a palliative measure for borate intoxication, agricultural practices recommend using (boron-free) organic corrections, such as the addition of nitrates that exhibit a certain ionic antagonism to borates, and calcium salts that precipitate boron in the form of relatively insoluble calcium borates. For this reason, fertilisation with $Ca(NO_3)_2$ is recommended.

2. OBJECTIVES

In this work the possibility was studied of using calcium oxide as an alternative precipitating agent to sodium hydroxide in treating wastewater from ceramic frit milling, given the greater insolubility of calcium borates. For this purpose, three ceramic frits that are widely used commercially in the ceramic sector were milled in a standard test: a twice-fire frit, a monoporosa wall tile frit, and an opaque frit for single-fire ceramic floor tile manufacture. The milling waters were characterised by the Jar-Test, and for their

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[1] P.S. HOVATTER AND R.H. ROSS, *A comparative analysis of the toxicity of boron compounds to freshwater and saltwater species,* Environmental toxicology and risk assesment, Third Volume; Jane Staveley Hughes, Gregory R. Biddinger, Eugene Mones Editors.

[2] LEY DE AGUAS 29/85 DE 2 DE AGOSTO, BOE 189 de 8 de Agosto.

[3] G. MONRÓS, M. LLUSAR, M.A. TENA, J. CALBO, *Análisis de los parámetros medioambientales de pastas para baldosas cerámicas de cocción roja o blanca,* Cerámica Información, 253, 42-66, 1999.

adequate coagulation-flocculation, an aqueous solution of NaOH and a commercial CaO powder were used. The quantity of borates present were measured by the azomethine method [4] in waters obtained by decantation, analysing the effectivity of the two precipitating agents used according to the type of ceramic matrix treated.

The purpose of the work was to characterise the milling water of the three ceramic frits from the viewpoint of the boron load and eco-toxicity, and to study the effect of precipitation with CaO and the addition of $Ca(NO_3)_2$ in the precipitation-decantation of these waters, comparing the results with the usual treatment process with NaOH.

3. EXPERIMENTAL DESIGN

Three widely used frits in ceramic floor and wall tile manufacture were chosen: a clear twice-fire frit, a clear monoporosa wall tile frit, and an opaque frit for single-fire stoneware floor tile manufacture. The characteristics of the frits used can be summed up as follows: the twice-fire frit was a clear boric frit (8-15% B_2O_3) with lead additions (3-10% PbO), the monoporosa frit was a calcium and zinc-based clear frit (about 10% CaO and ZnO) with the presence of about 5% ZrO_2 as well as B_2O_3 (between 3-6%), and finally, the opaque floor tile frit was rich in alumina (20%) with 10% alkali fluxes and low B_2O_3 contents (1-3%). Quartz was also treated according to the procedure set out below, with a view to having a reference blank without boron.

The various experimental procedures used are presented in the flow chart of Figure 1. The following experimental procedures were conducted:

(I) Characterisation of milling waste suspensions by the leaching test to determine the degree of toxicity of the slurries obtained with each frit.

(II) Characterisation of the waters from the precipitation-decantation of milling suspensions, to determine the possible differences on using different precipitating agents (NaOH or CaO) on the immobilisation-adsorption capability of the resulting sludges.

(III) Characterisation of the waters from the precipitation-decantation of milling suspensions with CaO in the presence of $Ca(NO_3)_2$ additions with a view to determining the effect of the agrochemical additive on the immobilisation-adsorption capability of the resulting sludges.

(IV) Characterisation of the waters from the centrifugation of the milling suspensions with CaO in the presence of additions of spent A-zeolite from petroleum cracking, with a view to determining the effect of this selective absorbent on the immobilisation-adsorption capability of the resulting sludges.

4. RESULTS AND DISCUSSION

To avoid any interference, the mills were cleaned prior to frit milling by milling quartz with 5% mannitol (to complex the boron that might be left and thus remove it from the mills) for 10 minutes, followed by rinsing with distilled water.

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[4] F.J. LÓPEZ, E. GIMÉNEZ, AND F. HERNÁNDEZ, *Analytical study of the determination of boron in environmental water samples*, Fresenius J. Anal Chem 346, 984-987, 1993.

The frits and reference blank were milled in planetary type mills with porcelain media for 1 hour at 800 r.p.m., using a frit/ball/water mass ratio = 100/90/60 . This was done by milling 300 g of each frit as well as the reference quartz, subsequently adding water to collect the frit rests left in the mill jars, collecting a total volume of 500 mL suspension. The characteristics of this suspension are presented in Table I. According to the results obtained all the suspensions presented an alkaline pH 9 and 10 owing to hydrolysis of the solubilised silicates and borates. The conductivity was much greater for the twice-fire frit than for the others, which exhibited similar levels, confirming the well-known fact of greater salt and frit solubilisation at low temperature.

	Quartz	**Clear twice-fire**	**Clear monoporosa**	**Opaque Stoneware**
d_{ap} (g/mL)	1.35	1.35	1.35	1.35
pH	7.4	10.4	8.8	9.8
Cond (μS)	177	2080	861	784

Table 1. *pH, density and conductivity of the millings.*

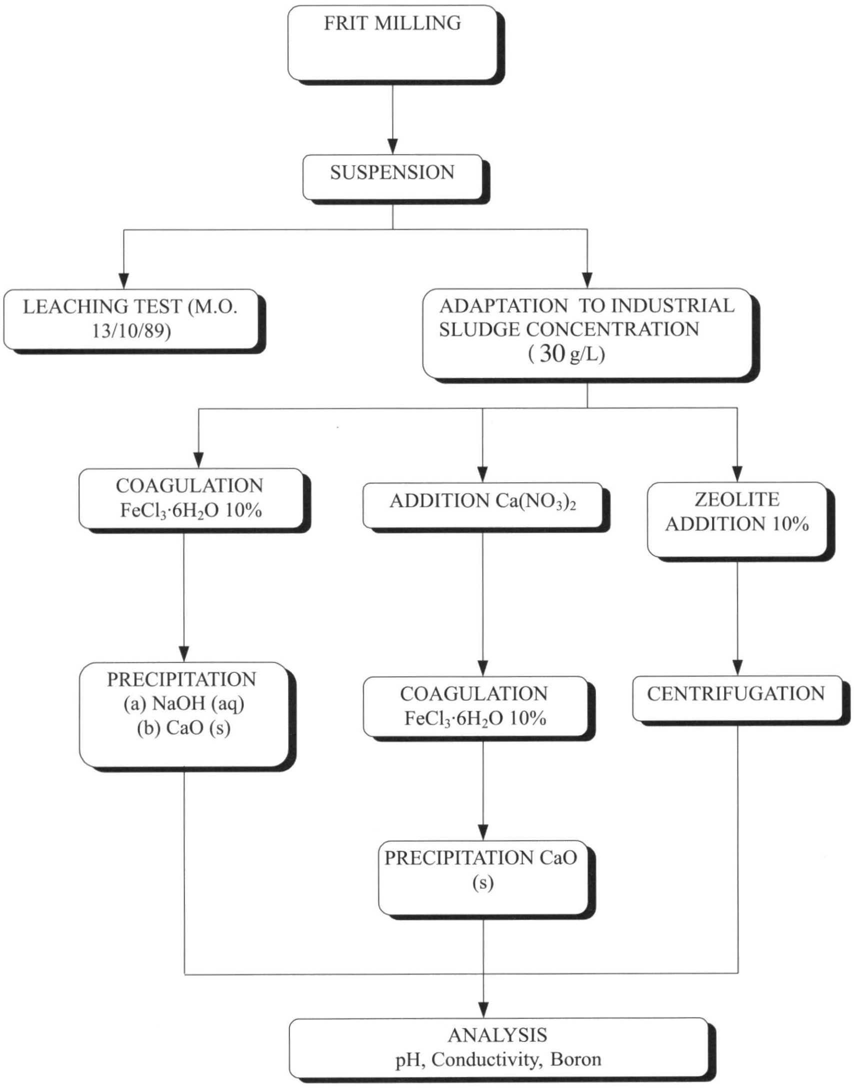

Figure 1. *Schematic illustration of the procedure followed.*

4.1. CHARACTERISATION OF MILLING WASTE SUSPENSIONS BY THE LEACHING TEST.

In accordance with procedure I of Figure 1, the suspensions obtained in milling frits considered as waste were subjected to the leaching test as set out in the Ministerial Order (M.O.) of 13/10/89 as Method 2 [5]: 40 g waste was mixed with 16 times its weight in distilled water and stirred at 4.5 pH, achieved by adding 0.5 M acetic acid under constant stirring for 24 h, after which the quantity of water was adjusted and filtered after a 30-min stand, thus obtaining the testing water.

The Jar-Test was conducted on these waters with a 50 mL solution to which different quantities of coagulant were added with 100 μl / 300 μl / 500 μl $FeCl_3.6H_2O$ at 10%, subsequently brought to 8.5 pH with NaOH in a 2.5% solution (procedure Ia) or commercial lime powder (procedure Ib). The boron concentration was measured on these waters, performing the Photobacter Phosphoreum inhibition biotest.

The Jar-Test data are set out in Table 2. Table 3 presents the analysis results of the decanted waters.

	Clear Tw. F. NaOH	Clear Tw. F. CaO	Clear S. F. NaOH	Clear S. F. CaO	Opaque stonew. NaOH	Opaque stonew. CaO	Quartz NaOH	Quartz CaO
pH								
100 *	4.3		4.9		5.2		-	
300	3.0		4.3		4.5		-	
500	2.9		3.4		3.5		2.7	
Clarification t (h)								
100 *	3.5	3.5	3.5	3.5	3.5	3.5	-	-
300	2	2	3.5	3.5	3.5	3.5	-	-
500	2	2	2	2	2	2	1	1
Sludge height (mm)								
100 *	6	6	8	9	8	7	-	-
300	8	9	10	11	9	10	-	-
500	9	10	12	12	11	10	11	11
Residual turbidity	NO	YES	NO	YES	in 100	YES	NO	NO
Optimum conditions*	300	100	100	100	100	100	-	-

(*) Flocculant addition: μl $FeCl_3.6H_2O$ at 10% /50mL sample.

Table 2. *Jar-Test data on the leaching test waters (procedure I).*

Table 2 data indicate acid pH in the waters with the coagulant, becoming more acid on raising this addition. The clarification time of the waters after adjusting the pH with NaOH or CaO decreased with the flocculant addition and was independent of the precipitating agent used. However, settled sludge compaction fell with the rise in flocculant, precipitation with NaOH exhibiting better results except in the case of the

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[5] ORDEN MINISTERIAL 13/10/89. *Métodos de caracterización de RTPs.*

opaque frit. The use of CaO impedes total clarification of the waters, which exhibited a certain residual turbidity. In general, optimum clarification conditions involved the use of small quantities of flocculant.

Table 3 data indicate that the boron concentration was quite high in the case of the clear twice-fire frit (53.4 ppm), being lower in the rest as was to be expected according to the frit formulation. The effect of precipitation with NaOH or with CaO only presented a certain effectivity in the case of the twice-fire frit (about 20% boron absorption in the precipitate), there being no differences between NaOH and CaO. The rise in flocculant did not affect borate absorption in the sludge and raised the quantity of precipitant required, with the ensuing rise in conductivity of the decanted waters.

	Clear Tw. F. NaOH	**Clear Tw. F. CaO**	**Clear S. F. NaOH**	**Clear S. F. CaO**	**Opaque stonew. NaOH**	**Opaque stonew. CaO**
pH	8.5	8.5	8.5	8.5	8.5	8.5
Cond (μS)						
100*	658	664	1281	1291	1011	1011
300	1070	1032	1716	1692	1569	1561
500	1634	1607	2120	2110	2010	1989
B(ppm) (water solids cont. 30g/L)	53.4		4.4		13.2	
B(ppm) (decanted waters)						
100 *	37	40	6	6	13	13
300	40	38	6	6	11	12
500	36	37	6	6	11	11
Inhibition biotest	Negative in all the samples					

Table 3. *Results in leaching test waters subjected to precipitation-decantation (procedure I).*

The required Photobacter Phosphoreum inhibition biotest laid down in M.O. 13/10/89 [5] was negative in all the samples.

In accordance with the results obtained, the leachates of the ceramic frit milling suspensions did not exhibit any inhibition in the eco-toxicity test with Photobacter Phosphoreum and the boron levels were only significant in the case of the twice-fire frits.

4.2. CHARACTERISATION OF THE WATERS FROM PRECIPITATION-DECANTATION OF THE MILLING SUSPENSIONS.

In procedures II, III and IV of Figure 1, the master waters were diluted 20 times to achieve a level of solids concentration of around 30g/L. At this dilution level, a higher solids concentration was found than expected for a ceramic industry type of waste (about 20 g/L). The water balances in the sector [6] indicate that considering a

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[5] ORDEN MINISTERIAL 13/10/89. *Métodos de caracterización de RTPs.*

[6] J.E. ENRIQUE, E. MONFORT, F. FERRANDO, Mª F. GAZULLA, *Boron air emissions in glazed tile manufacturing processes with total waste reuse,* Qualicer 98, Pos-65, Vol. II.

mass of 18 kg for 1 m^2 product, total process water consumption would be 19.1 L/m^2: 41% is released into the air in the spray-drying and drying stages, so that the wastewater flow rate would be about 11.3 L/m^2. Assuming that on average 1 kg glaze/m^2 is involved and that the proportion of sludge produced in the glazing machine is 10% (0.1 kg/m^2), the solids loading in the wastewater would be about 9 g/L. Assuming that water-saving measures could manage to halve wastewater production, which is improbable though possible (company data indicate between 9 and 15 L/m^2), working conditions would be around 20g/L: in this case a higher solids loading was chosen to obtain more representative results.

The milling suspension obtained as set out in point 4 and diluted to a solids concentration of 30 g/L was subjected to a Jar-Test: different coagulant additions with 200 μl / 400 μl / 600 μl $FeCl_3 \cdot 6H_2O$ at 10% were made to 50 mL solution, and subsequently alkalinised to pH 8.5 with the precipitating agent used: NaOH in a 2.5% solution and commercial lime powder. The sample was stirred the whole time, which was extended until half an hour after adding the precipitating agent. To monitor sludge decantation, the suspension was poured in a glass test tube with a 27 mm diameter, where the height of the deposited sludges was monitored with time. After establishing optimum precipitation conditions, these conditions were applied to the reference blank obtained with quartz.

	Clear Tw. F. NaOH	Clear Tw. F. CaO	Clear S. F. NaOH	Clear S. F. CaO	Opaque stonew. NaOH	Opaque stonew. CaO	Quartz NaOH	Quartz CaO
pH								
200 *	3.6		6.2		6.0		-	
400	3.2		3.6		3.4		-	
600	3.0		3.2		3.1		2.9	
Clarification t. (h)								
200 *	no	3.5	no	3.5	no	3.5	-	-
400	3.5	3.5	3.5	2	3.5	3.5	-	-
600	3.5	3.5	2	2	3.5	2	1	1
Sludge height (mm)								
200 *	-	6	-	10	-	8	-	-
400	10	9	12	12	11	11	-	-
600	12	10	12	13	11	11	11	11
Residual turbidity	NO	in 200 and 400	NO	NO	NO	en 200	NO	NO
Optimum conditions*	400	200	600	200	400	200	-	-

(*) Deflocculant addition: µl $FeCl_3 . 6H_2O$ at 10% /50mL sample.

Table 4. *Jar-Test data (procedure II).*

Table 4 presents the Jar-Test data. Table 5 sets out the analysis results.

The data obtained do not differ from the previous leaching test. The Jar-Test indicates shorter clarification times with the use of CaO, while the sludges appear to compact better with CaO although problems of slight turbidity persist with this precipitant.

	Clear Tw. F. NaOH	**Clear Tw. F. CaO**	**Clear S. F. NaOH**	**Clear S. F. CaO**	**Opaque stonew. NaOH**	**Opaque stonew. CaO**	**Quartz NaOH**	**Quartz CaO**
pH	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
Cond (μS)								
200*	-	560	-	695	-	575		
400	973	956	1075	1062	957	995		
600	1500	1530	1620	1565	1513	1524		
B (ppm) **(water solids cont. 30g/L)**	53.4		4.4		13.2			
B(ppm)								
200 *	-	**41**	-	**4**	-	**7**	-	-
400	**34**	37	4	5	**9**	10	-	-
600	33	41	**4**	5	8	10	0	0
Pb (ppm)								
200*	-	N.D.	-	N.D.	-	N.D.		
400	N.D.	-	-	-	N.D.	-		
600	-	-	N.D.	-	-	-		
Inhibition biotest	Negative in all the samples.							

Table 5. Decanted water data of procedure II.

Boron analysis with azomethine in the clarified waters exhibited similar results to those found in the leaching study. Significant borate absorption in the sludge was only found with the twice-fire frit (about 20%). More salts could in principle be expected to solubilise on leaching the sludges for 24 hours in acetic medium. This was in fact the case as comparison of the conductivities of the flocculant additions in Tables 2 and 4 shows, being larger in waters subjected to acetic leaching. However the analysed borate rates were the same in the two treatments. In reality, frit solubilisation in milling follows fast saturation kinetics [7], so that it all practically solubilises in the first five minutes of milling, which explains the insignificant effect of boron solubilisation in the acetic leaching operation.

The clarified waters did not present any inhibition in the Photobacter Phosphoreum inhibition biotest. Nor was any lead detected in these waters by atomic absorption.

4.3. CHARACTERISATION OF WATERS FROM PRECIPITATION-DECANTATION OF MILLING SUSPENSIONS WITH CaO IN THE PRESENCE OF $Ca(NO_3)_2$ ADDITIONS.

In procedure III of Figure 1, the foregoing study was repeated, in this case adding $Ca(NO_3)_2$ (2.1 mmol/L, 4.2 mmol/L and 6.3 mmol/L which involve borate:calcium molar

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[7] F. SANMIGUEL, V. FERRANDO, J.L. AMORÓS, M.J. ORTS, M.F. GAZULLA, P. GÓMEZ, *Solubilidad de fritas en Suspensiones de esmalte. Influencia de algunas variables de operaciones sobre la cinética del proceso,* Técnica Cerámica, 275, 689-700,1999.

ratios =1:2, 1:4 and 1:6 respectively for samples with 50 ppm boron) to the milling waters, with a view to analysing the possible effect on borate absorption, presumably favoured by borate precipitation in the form of the relatively insoluble calcium borates.

Only the addition of the optimum flocculant in the study in point 4.2 was used. The results are given in Table VI, showing that the presence of $Ca(NO_3)_2$ did not improve absorption in the boron precipitates. In fact, the twice-fire sample, which in the foregoing studies retained 20% did not retain anything in the presence of the $Ca(NO_3)_2$ electrolyte. The presence of this electrolyte appeared to negatively modify sludge absorption equilibrium independently of the arising insolubilisation.

Type of Frit	Boron concentration (ppm)			
	Non-cleaned frit	Zeolite addition (10%)	Calcium nitrate *(mmol/50mL)	
Clear twice-fire	53.4	59.2	*0.105	52.8
			*0.210	53.4
			*0.315	54.9
Opaque stoneware	13.2	10.4	*0.105	8.6
			*0.210	9.5
			*0.315	8.7
Clear monoporosa	4.4	7.0	*0.105	5.9
			*0.210	5.8
			*0.315	6.5

Table 6. *Results of the calcium nitrate (procedure III) and zeolite addition (procedure IV).*

4.4. CHARACTERISATION OF WATERS FROM MILLING SUSPENSION CENTRIFUGATION WITH CaO IN THE PRESENCE OF AN ADDITION OF SPENT A-ZEOLITE FROM PETROLEUM CRACKING.

In procedure IV of Figure 1, study 4.2 is repeated but in this case with the 10% addition (in respect of the milled frit) to the milling suspension of a spent A-zeolite from an FCC catalytic cracking process, supplied by B.P. petrochemicals in Castellón. This waste material with a definite composition exhibits a relative absorption and ion-exchange capability detected elsewhere [8].

The frit milling suspension with the zeolite was stirred for 30 minutes, separating the solids by centrifugation. Boron was measured in the clarified waters by the azomethine method. Table VI presents the results, indicating that the zeolite used was not effective in absorbing borates. The centrifuged waters exhibited a certain turbidity, which could have raised the measured borate quantities slightly.

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[8] M.C. GRAÑANA, *Reutilització de residus de cracking petrolifer en la producció de pigments ceràmics,* Degree Thesis, Universitat Jaume I, September 1997.

5. CONCLUSIONS

The following conclusions were drawn from the study:

(1) Ceramic frit milling suspensions, characterised as waste according to Ministerial Order 13/10/89, yield a negative result in the Photobacter Phosphoreum inhibition test and only the twice-fire frits add borate quantities to the milling stage exceeding the limit in Table 1 for emissions of the Regulations for the Protection of the Hydraulic Public Dominion.

(2) The use of traditional precipitation-decantation systems with NaOH reduces the borate rates by up to 20% in the waters, precipitating all the lead, which is not detected by atomic absorption.

(3) The use of CaO in the precipitation-decantation process instead of NaOH presents very similar results to that of borate and lead absorption. The Jar-Test indicates shorter clarification times with the use of CaO, and the sludges appear to compact better with CaO though the waters exhibit a certain residual turbidity compared to waters treated with NaOH.

(4) The addition of $Ca(NO_3)_2$, used as a palliative fertiliser with regard to the toxic effects of borates in citriculture, in the stage before precipitation-decantation with CaO, reduces the sludge absorption capability. The use of a spent A-zeolite from catalytic cracking processes as a borate-absorbing additive had no significant effect.