The Removal of Fe, Zn, Cu, and Pb from Wastewaters Using Chabazite Zeolites Produced from Southern Brazilian Coal Ashes

Júlio César Trois Endres, Lizete Senandes Ferret, Iolanda Dill Fernandes and Luciana Campos Hofmeister

Fundação de Ciência e Tecnologia – CIENTEC
Rua Washington Luiz, 675, CEP 90.010-460, Porto Alegre, RS, Brazil
Phone: ++51-3287-2000, Fax: ++51-2226-0207
Email: processos@cientec.rs.gov.br

KEYWORDS: zeolites, water treatment, metal removal

ABSTRACT
The use of the southern Brazilian coal ashes generated in power plants for the production of zeolites can constitute an alternative and noble use for a residue which has historically contributed for the degrading of vast areas. Brazilian's largest coal mine – Candiota – is located in the state of Rio Grande do Sul close to the borderline with Uruguai. The practice in Candiota, an open pit mine, is to use exhausted areas for the disposal of the ashes not commercialized (around 70%). As far as the disposal of ashes is concerned, a good improvement has been done, particularly during the last 5 years, with the adoption of proper techniques for the soil recovery. Despite that, the presence of old deposits dating from the sixties associated with the natural conditions of the surrounding soil has contributed to the contamination of the region´s surface waters, particularly with metals. It is shown here that a Chabazite zeolite can be used for the reduction of the region's water metal content with good results. That is, the region's main residue is used for the production of a material which can help to reduce the environmental impact associated to its disposal.

INTRODUCTION

The use of both natural and synthetic zeolites for the removal of cations from aqueous solutions have extensively reviewed by, respectively, Ouki and Kavanaugh[1], and Querol *et al*.[2,3,4] and will not be repeated here. This work, however, focus on the production of zeolites using fly ashes as raw material and its capability for the removal of cations from aqueous solutions.

Brazilian coals are characterized among other things for high ash contents (45-55%, w/w). Despite the fact that there are several uses (cement, civil construction artefacts, etc.) for the ashes generated, particularly for those generated in large units (power generation), around 70% of the total is returned to exhausted mine pits. For this purpose, a search for new applications for this residue is underway. The production of zeolites from the coal ashes produced could constitute, as a consequence, an alternative and noble use for a residue which has historically contributed for the degradation of large areas located in the Brazilian state of Rio Grande do Sul. As far as the disposal of fly ashes is concerned, a good improvement

has been done, particularly over the last 5 years, with the adoption of proper techniques for soil recovery. Despite that, the presence of old deposits dating from the sixties associated with the natural conditions of the surrounding soil has contributed to the contamination of the region´s surface waters, particularly with metals. It is shown here that a Chabazite-based zeolite can be used for the reduction of the region's water metal contents with good results. That is, the region's main residue is used for the production of a material which can help reducing environmental damage associated with the generation of the residue itself.

Adopting a procedure detailed on early papers, Ferret *et al* [5] and Fernandes *et al.*[6], southern Brazilian coal fly ashes were subjected to a treatment which consisted, basicaly, to a reaction with NaOH (3.5N) at 100 ^{o}C for 72h, followed by cooling, washing, centrifugation and drying. The crystalline structures obtained are composed mainly by Chabazite, Faujasite, Cancrinite and Hydroxisodalite-type zeolites, with the predominance of Chabazite.

The zeolites produced were later tested for the removal of Fe, Zn, Cu, and Pb from solutions whose concentrations ranged between 2,8 and 54 ppm. The overall removal efficiency, for contact times ranging between 1 and 24h, was 91%.

EXPERIMENTAL SECTION

Materials

The zeolites used in the study were synthetized using fly-ashes produced on a large scale coal-fired power plant used for electricity generation purposes. The coal comes from the Candiota Mine, located just 2 miles from the plant. The Candiota Mine is Brazil's largest coal reserve and the power generation unit located in the region contributes with approximately 50% of the total amount of ashes (fly + bottom) produced in the country. The annual production of coal ashes in Brazil ranges around 1.7 x 10^6 tons, but this figure might reach 4.0 x10^6 tons by year 2005. Table 1 shows proximate and ultimate analyses of the Candiota Coal. Coal proximate and ultimate analyses carried out according to, respectively, ASTM D3172 and ASTM D5373.

Table 1 - Candiota Coal, proximate and ultimate analyses.

Ash content, % (dry basis, w/w)	56.2
Carbon content, % (dry basis, w/w)	31.6
High heat value, kcal/kg (dry basis)	2,945
Sulphur content, % (dry basis, w/w)	1.13
Total moisture, %	17.8
Volatile matter, % (dry basis)	18.7

The combustion of the Brazilian coals and particularly the Candiota coal produces, as a rule, fly ashes with high SiO_2 and Al_2O_3 contents. The sum SiO_2+Al_2O_3 is regarded as of paramount importance for zeolification purposes. The basic composition of the ashes, on the other hand, is presented in Table 2. Coal ash content and ash composition analyses carried out according to, respectively, ASTM D3174 and ASTM D4326.

Table 2 - Candiota Coal ashes, basic chemical composition.

Component	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	MgO	CaO	P_2O_5
%	67.5	18.7	3.63	0.17	1.83	0.70	0.20	1.72	0.09

Synthesis

The ash samples were activated by means of a NaOH (3.5N) solution in an opened system. The zeolite conversion was carried out at 100ºC and the reaction time was 3 days. The activation was performed using a sample concentration of 0.125g/mL. The tests were performed in teflon covered laboratory reactors. When the activation time was reached, the sample was centrifuged, filtered, washed with deionized water and dried at 105ºC for a 24-hour period. The samples were finally analyzed by X-ray diffraction. For a 3-day reaction time Faujasite and particularly Chabazite were the main crystalline structures formed, as presented in scanning electronic microscope – SEM photographs shown in Figure 1.

Ion Exchange Tests

The cation exchange tests were carried out upon metals selected not randomly but taking into account their importance locally. Locally, in the context of the work carried out, means some of the metals whose concentrations might somehow have contributed to the deterioration of the areas surrounding the Candiota coal minefield. For this purpose the metals, whose removal from aqueous solutions were studied, are Fe, Zn, Cu, and Pb. The concentrations of these metals found in some of the region's surface waters, particularly in those most affected, were found to be sometimes fivefold the limits established by the local environmental agencies, despite the measures adopted in the region for the protection of those surface water bodies.

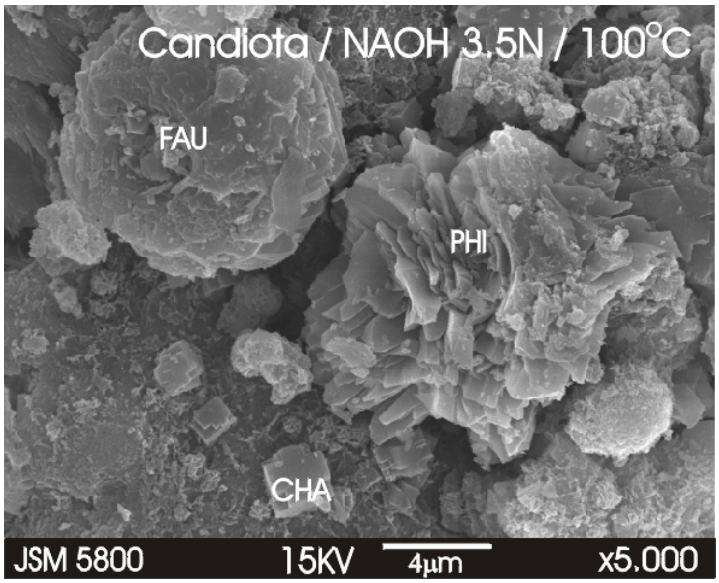
The tests were carried out for metal concentrations ranging between 2,8 and 54 ppm The metal solutions were prepared either from their respective salts or from standardized solutions. The contact times were 1, 2, 3 and 24 hours. The metal removal was tested for three different media, i.e., acid, alkaline and neutral. The ratio zeolite/solution adopted was 1:100. As soon as the contact time was elapsed the samples were filtered and the metal-depleted solutions analyzed by either atomic absorption or titration. The latter technique was adopted only for Fe determinations.

RESULTS AND DISCUSSION

The relevant data obtained as part of the tests performed upon metal removal are presented in Tables 3 and 4. The results of the metal removal analyses, particularly those obtained in acid medium, are shown in Figure 2.

Acid medium

The results obtained, particularly for a 1-hour contact time suggest that the Chabazite-type zeolite produced under the conditions explained earlier, could be used for water treatment purposes. The overall removal efficiency, for 1, 2 and 24-hour contact time, were, respectively, 88, 80 and 92%. The overall removal efficiency obtained for a 2-hour contact time - 80% - came as a surprise and, despite the scarcity of the data obtained, is possibly associated to the alkalinity of the zeolite produced. That is, an initial change upon the pH of the aqueous solution is followed by effect expected with Na sodium been replaced by the other metals. The results obtained, despite preliminary, showed, for the metals and concentrations tested, a very good removal efficiency which suggests that the study should be complemented. The tests will be repeated in order to check for reproducibility and different concentrations are expected to be tested.



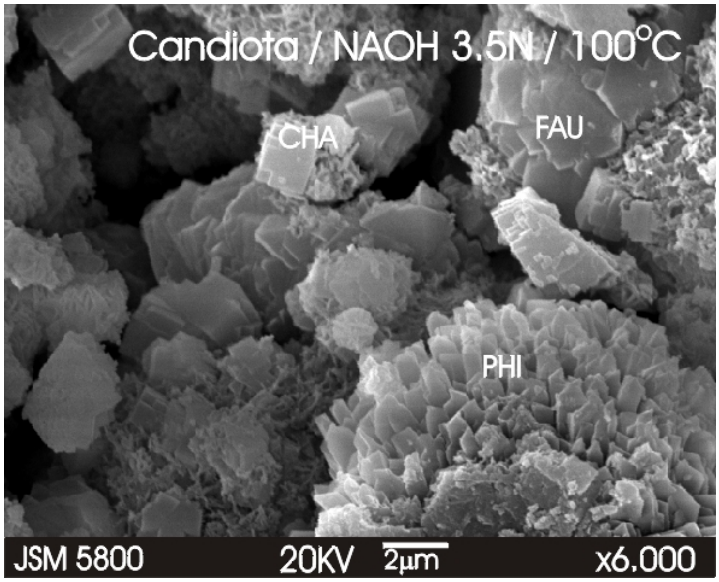
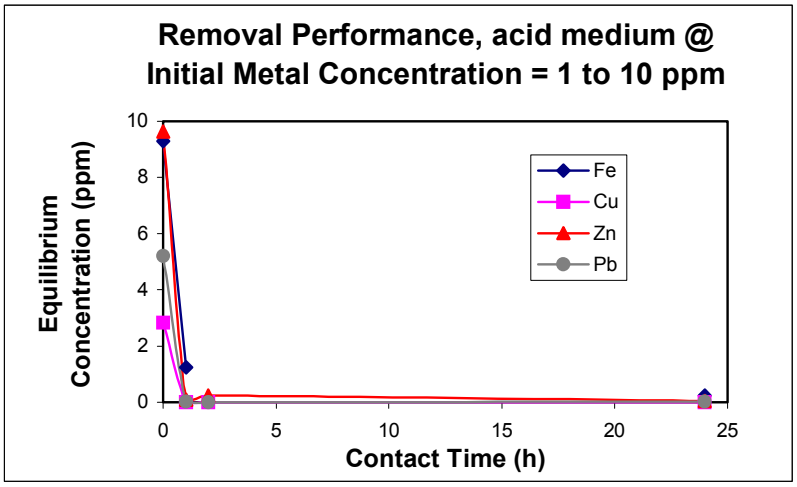
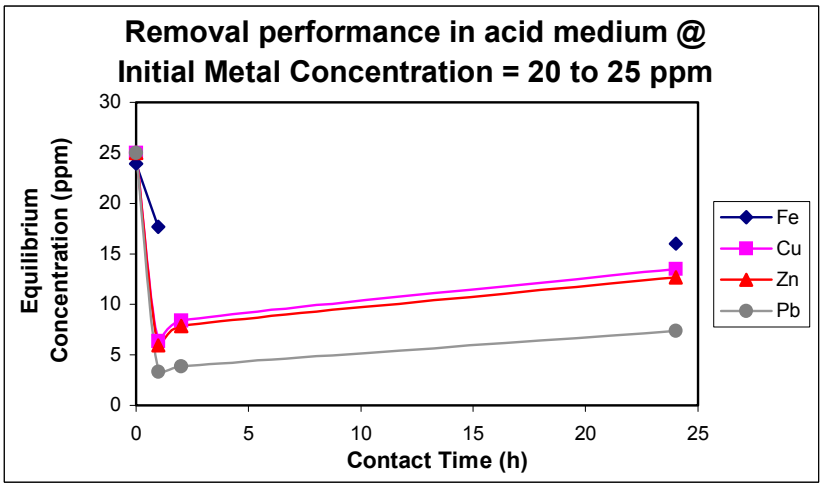


Figure 1 – Zeolite crystalline structures.





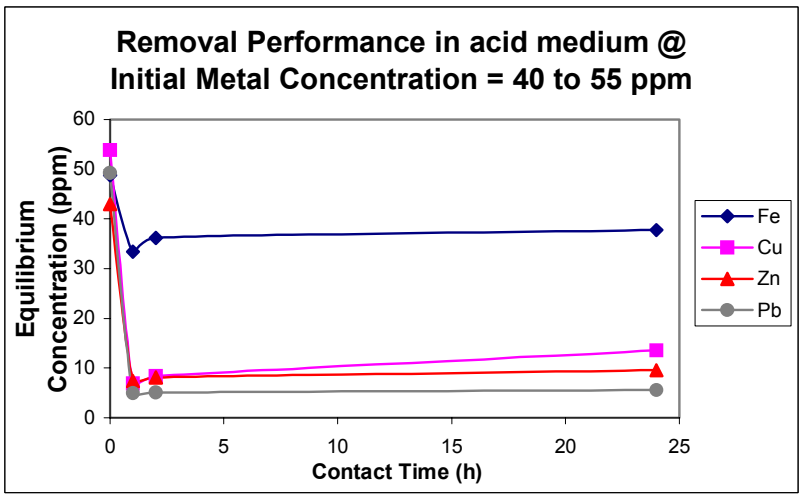


Figure 2 – Metal removal perfomance, acid medium, all concentrations

Table 3 - Metal removal, acid medium.

Metal	Fe			Cu			Zn			Pb		
Contact time, h	Initial and final concentrations (ppm), removal percentage											
-	9,3	23,9	48,8	2,83	25,0	53,8	9,64	25,0	43,0	5,20	25,0	49,2
1h	1,24	3,0	1,65	<LD	0,27	21,1	0,09	0,81	28,8	0,024	0,2	0,2
	87%	87%	97%	100%	99%	61%	99%	97%	33%	100%	99%	100%
2h	-	-	-	0,008	14,2	7,09	0,24	16,3	17,5	0,005	0,3	0,12
				100%	43%	87%	98%	35%	59%	100%	99%	100%
24h	0,24	0,65	0,65	0,003	0,57	12,6	0,05	1,85	22,0	0,018	0,14	0,11
	97%	97%	99%	100%	98%	77%	99%	93%	49%	100%	99%	100%

Alkaline medium

Here too, good removal efficiencies were observed, but particularly for Zn, Pb e Cu. The overall removal efficiency obtained, averaged for all data obtained (four metals) and for 1, 2 and 24-hour contact times, were, respectively, 72, 89 and 67%. The results suggest that the pH of the medium plays a role here, if one compares the data found here with those reported in the previous section. The differences observed in terms of removal eficciency are obviously explained by the propriety presented by acid solutions to fix metals and needs no further explanation. Besides, it is worth mentioning here that zeolites produced according to the method preconized here are expected to be tested with coal mine wastewaters, currents characterized amongst other things for their low pHs.

Table 4 - Metal removal, alkaline medium.

Metal	Fe			Cu			Zn			Pb		
Contact time, h	Initial and final concentrations (ppm), removal percentage											
-	9,3	23,9	48,8	2,83	25	53,8	9,64	25	43,0	5,20	25	49,2
1h	8,4	17,7	33,4	0,036	6,38	6,90	0,120	5,95	7,38	0,037	3,31	4,99
	10%	26%	32%	98%	74%	87%	99%	76%	83%	99%	87%	90%
2h	-	-	36,2	0,029	8,40	8,40	0,106	7,86	8,06	0,043	3,86	5,14
			26%	99%	66%	84%	99%	69%	81%	99%	85%	90%
24h	5,8	16,0	37,8	0,034	13,5	9,80	0,066	12,7	9,53	0,050	7,38	5,61
	38%	33%	22%	99%	46%	82%	99%	49%	78%	99%	70%	89%

CONCLUSIONS

The present study shows that use of zeolites produced from Candiota flyashes can be used applied to the removal of metals from aqueous solutions with very good efficiency. The results obtained, particularly for short contact times suggests that the use Chabazite-type zeolites for the removal of metals from aqueous solutions might as well find different industrial applications than those addressed here.

ACKNOWLEDGEMENTS

The authors wish to thank both the Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul - FAPERGS and the Fundação de Ciência e Tecnologia – CIENTEC their financial support, without which this research would not be possible.

REFERENCES

[1] Ouki, S.K. and Kavannagh, M., Water Science Technology, 1999, 39 (10-11), p.115.

[2] Querol, X., Plana, F., Alastuey, A. and López-Soler, A., *Fuel*, 1997, 76 (8), p. 793.

[3] Querol, X., Plana, F., Umana, J., Alastuey, A., López-Soler, A. and Tartera, J., *8th Australian Coal Science Conference*, 1998.

[4] Querol, X., Umana, J., Alastuey, A., Bertrana, C., López-Soler, A. and Plana, F., Energy Sources, 1999, in press.

[5] Fernandes, I.D., Ferret, L.S., Krahl, C.A., Endres, J.C.T. e Maegawa, A., *International Ash Utilization Symposium,* Lexington, Kentucky, EUA, 1999.

[6] Ferret, L.S., Fernandes, I. D., Ferret, L. S., Krahl, C. A ., Endres, J.C.T. e Maegawa, A., *International Ash Utilization Symposium*, Lexington, Kentucky, EUA, 1999.