

# Proposal of a Methodology for the Preliminary Assessment of Kaolinitic Clay Deposits as a Source of SCMs

Adrián Alujas Díaz<sup>1(✉)</sup>, Roger S Almenares Reyes<sup>2</sup>, Florencio Arcial Carratalá<sup>3</sup>, and José F. Martirena Hernández<sup>4</sup>

<sup>1</sup> Centro de Estudios de Química Aplicada, Universidad Central de Las Villas, 54830 Santa Clara, Cuba

<sup>2</sup> Departamento de Metalurgia – Química, Instituto Superior Minero Metalúrgico de Moa, 83330 Moa, Cuba

<sup>3</sup> Empresa Geominera del Centro, 54800 Santa Clara, Cuba

<sup>4</sup> Centro de Investigación y Desarrollo de Estructuras y Materiales, Universidad Central de Las Villas, 54830 Santa Clara, Cuba

**Abstract.** The growing interest in calcined clays as Supplementary Cementitious Materials (SCMs), from sources other than relatively pure industrial grade clay deposits, demands the development of new tools for the identification and evaluation of the potentialities of a given clay deposit as a source of raw materials for the production of SCMs. In this paper, a methodology for the preliminary assessment of kaolinitic clay deposits as a source of SCMs is presented and discussed. As a case study, the chemical and mineralogical composition of several non industrial grade kaolinitic clay deposits, identified and classified according to the proposed methodology, is related to the pozzolanic reactivity of their calcination products. The developed methodology allows to establish preliminary selection criteria based on the chemical composition of the raw material ( $\% \text{Al}_2\text{O}_3 > 18,0$ ;  $\text{Al}_2\text{O}_3/\text{SiO}_2 > 0,3$ ;  $\text{LOI} > 7,0$ ;  $\% \text{CaO} < 3,0$ ;  $\% \text{SO}_3 < 3,0$ ). Comparison of the potentialities between the different clay deposits is determined from its relative position in a plot that relates the content of  $\text{Al}_2\text{O}_3$  and the weight loss within the range of temperatures that corresponds to the thermal decomposition of clay minerals, which are, in turn, the main parameters affecting the pozzolanic reactivity of calcination products. The presence of thermally active non clay minerals in the sample may also affects negatively the pozzolanic reactivity. Through the observed results, the developed methodology proves to be a practical and useful tool for the identification and evaluation of kaolinitic clay deposits as a source of pozzolans.

## 1 Introduction

At a global level, the production of pozzolanic materials from calcined clays focuses primarily on the use of industrial grade kaolin, ignoring the possibilities offered by low grade kaolinitic clay deposits with high degree of impurities, highly abundant in tropical and subtropical areas, where their identified and hypothetical resources exceed billions of tons [1]. This is partly because the current approach for the categorization of kaolinitic

clay deposits and estimation of their reserves responds to criteria derived mainly from the ceramics, paper or pigment industries, where selection parameters are very rigorous as regards to the absence of mineral impurities that may affect color and plasticity [2, 3]. The absence of selection criteria adapted to the evaluation of the potentialities of clay deposits as a source of raw materials for obtaining pozzolanic materials, limits their identification and exploitation on an industrial scale. In this way, the present work is directed towards the development and application of a procedure for the preliminary evaluation of the potentialities of clay deposits as a source of SCM.

## 2 Analysis and Discussion

Given the relative heterogeneity of chemical and mineralogical composition of clay deposits, it is necessary to identify those essential parameters that influence the behavior of the clays as source of pozzolans. From the results of several research it can be concluded that the most important parameter in the pozzolanic reactivity of calcined clays is their content of clay minerals, more specifically their content of minerals from the kaolinite group, which must be equal to or higher than 40% by weight [4, 5]. A material whose theoretical composition is 40% by weight of minerals of the group of kaolinite and 60% of quartz as an inert material will have a theoretical composition with no less than 15.80%  $\text{Al}_2\text{O}_3$ , an  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio of approximately 0.20 and LOI values of no less than 5.58. Based on this calculated values for chemical composition and also in practical experience on the analysis of the different kaolinite clays included in this research (Table 1) and other clay materials reported in previous studies [6, 7], the following parameters could be established as empirical selection criteria:  $\text{Al}_2\text{O}_3 \geq 18.00\%$ ;  $\text{Al}_2\text{O}_3/\text{SiO}_2 \geq 0.30$  and  $\text{LOI} \geq 7.00\%$ . In this analysis, it is also necessary to take into account the influence of the accompanying minerals in the pozzolanic reactivity of the final product. For the case of calcite, a negative effect on the pozzolanic reactivity has been reported at calcination temperatures above 800 °C, related to the formation of vitreous phases rich in Ca, Si and Al, of low specific surface area. This phenomenon has been extensively reported in the field of ceramic materials, where it is frequent to add small amounts of calcite to the kaolinite clays to increase the density of the calcination product. Negative effects on the degree of calcination of the final product have also been observed by the authors of this work for samples with relatively high pyrite content. In addition, both the decomposition of sulfides and the decomposition of sulfates during thermal activation generate undesirable  $\text{SO}_3$  emissions into the atmosphere, with a negative environmental impact. Therefore, it is proposed to limit the allowed maximum values of  $\text{SO}_3$  and CaO to 3.0%. Thus, the chemical composition criteria for accepting or rejecting a clay deposit as source of SCM are as follows:  $\text{Al}_2\text{O}_3 \geq 18.00\%$ ;  $\text{Al}_2\text{O}_3/\text{SiO}_2 \geq 0.30$ ,  $\text{LOI} \geq 7.00\%$ ,  $\text{SO}_3 \leq 3.0\%$  and  $\text{CaO} \leq 3.0\%$ .

**Table 1.** Chemical composition of analyzed clays

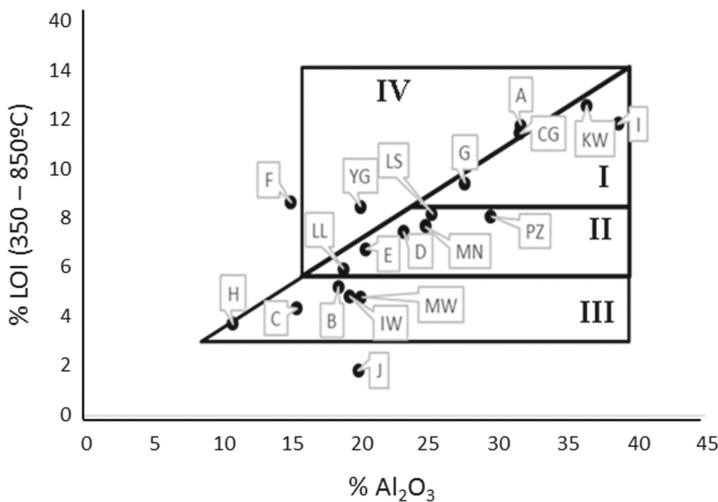
Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Others	LOI
MN	57,79	18,71	7,07	1,85	1,80	0,02	2,68	0,65	0,88	8,57
PZ	48,40	29,50	16,50	0,40	1,00	1,10	-	0,70	0,70	8,60
KW	48,00	36,40	0,85	0,14	0,11	0,03	0,02	0,48	0,56	13,41
IW	58,68	19,25	5,04	1,29	2,50	0,17	0,19	6,12	1,05	5,71
MW	63,15	20,09	3,96	1,15	2,27	0,51	2,22	0,54	0,22	5,90
LL	61,40	18,86	9,61	0,07	0,15	0,02	0,26	0,90	0,99	7,80
LS	50,88	25,23	12,58	0,28	0,95	0,02	0,08	0,32	1,26	8,39
YG	46,58	20,06	14,41	2,94	0,74	0,04	0,11	0,06	1,84	12,74
CG	39,55	31,58	12,68	0,05	0,53	0,13	0,14	0,17	0,94	14,37
A	46,96	31,66	5,81	0,14	0,06	0,02	0,02	0,11	0,82	14,44
B	60,33	18,44	6,49	1,03	1,95	0,01	1,64	1,41	1,40	7,38
C	64,34	15,44	9,91	0,08	0,48	0,01	0,15	0,65	1,52	7,49
D	63,95	23,15	1,49	0,07	0,09	0,00	0,02	0,02	0,73	10,53
E	64,61	20,45	4,64	0,15	0,39	0,01	0,03	0,93	0,81	8,03
F	55,75	15,01	5,98	7,09	1,22	0,55	0,58	2,00	1,72	10,31
G	53,78	31,83	8,89	0,91	0,03	0,00	0,00	0,50	1,90	10,84
H	54,74	18,32	4,91	0,41	0,00	0,00	0,00	0,22	1,29	4,66
I	43,25	38,71	1,53	0,10	0,00	0,01	0,12	0,06	3,52	11,70

For the quantification of clay minerals, the weight loss associated with dehydroxylation in the temperature range between 350 and 850 °C [8] is taken as the main criterion. Although some 2:1 clay minerals continue their dehydroxylation process at temperatures above 850 °C, for kaolinite clays the use of calcination temperatures above 850 °C is unusual, since the beginning of the recrystallization processes occurs at temperatures close to 900 °C. On the other hand, limiting the analysis interval to lower temperatures, although allows to quantify most of the contribution of 1:1 clay minerals, discriminates the possible contribution of other clay phases present in the analyzed material and makes the method unsuitable for 2:1 clays. However, even with high accuracy thermal analysis and careful data treatment it is very difficult to separate the individual contribution to the weight loss of each one of the clay minerals presents in the sample. Based on the fact that contributions to weight loss and pozzolanic reactivity is higher for minerals of the kaolinite group, and by assuming that weight loss in the temperature range between 350 and 850 °C are mainly related to kaolinite, the total content of clay minerals could be reported in terms of kaolinite equivalent (KEQ), as calculated by Eq. 1, where 0.1396 is the weight fraction corresponding to hydroxyl groups in kaolinite. Ultimately, the structural disorder is directly proportional to the loss of structural hydroxyls and directly related to the pozzolanic reactivity of the calcined clay.

$$\%KEQ = \frac{m(350^{\circ}C) - m(850^{\circ}C)}{m(200^{\circ}C) * 0.1396} \cdot 100 \quad (1)$$

In the quantification of weight losses, it is also necessary to consider the possible interference caused by the overlapping of the decomposition reactions of associated non-clay minerals. Among the most frequent associated non-clay minerals in clay deposits

are carbonates, sulphides, sulphates and hydroxides. These non-clay minerals, although decomposed in a relatively narrow range of temperatures, may have a significant influence on weight losses. However, as in relation to other clay and non-clay minerals, the minerals of the kaolinite group have a relatively high content of  $\text{Al}_2\text{O}_3$  (~39.50%), it is proposed to correlate the results derived from the quantitative analysis by weight losses with the content of  $\text{Al}_2\text{O}_3$  in the sample, to correct the possible interferences of the non-clay minerals. This could be expressed in the form of a graph represented in Fig. 1, in which the  $\text{Al}_2\text{O}_3$  content is related to weight losses. Diagonal line in the graph indicates the linear relationship between both parameters for minerals of the kaolinite group and also indicates the maximum value that the weight losses associated with the clay minerals can take in relation to the content of  $\text{Al}_2\text{O}_3$ . For samples whose composition places them below diagonal line, their content of clay minerals, expressed as %KEQ, is obtained by extrapolating their location to the line, from a line parallel to the axis of the  $\text{Al}_2\text{O}_3$  content. The location of samples above diagonal line indicates the presence of thermally active non-clay minerals in the range of 350 to 850 °C (carbonates, sulphates, sulphides, hydroxides). In this case, weight losses should be corrected to avoid overestimation of the content of clay minerals.



**Fig. 1.** Representation of several clay samples in a  $\text{Al}_2\text{O}_3$  vs LOI plot

Taking into account the characteristics of the sample as a function of the content of clay minerals, the graph represented in Fig. 1 could be divided into four zones, each one with distinctive characteristics. Region I includes those clays with relatively high kaolinitic clay contents ( $\text{KEQ} > 60\%$ ), and therefore, excellent potentialities of being used as a source of SCM. These clays may or may not contain relatively high amounts of iron-rich phases; therefore, this region of the diagram includes, but is not limited, to the so-called industrial grade kaolin. Samples in Region II are also representative of kaolinitic clays with good potentialities as a source of SCM, but with lower kaolinite contents ( $40\% < \text{KEQ} < 60\%$ ). In these zones of the diagram the vast majority of kaolinitic clay

deposits yet to be evaluated should be located. Zone III of the diagram refers to those clays with low kaolinite content ( $KEQ < 40\%$ ), but with relatively high content of 2:1 clays. It should be noted that, although this type of material does not generally meet the minimum selection criteria proposed for kaolinitic clays, it could be exploited as an alternative source of SCM in countries where the presence of kaolinitic clay deposits is relatively scarce [9, 10]. Finally, zone IV of the diagram includes clay deposits containing variable amounts of kaolinitic clay minerals, but with an appreciable content of non-clay minerals that decompose in the same temperature range than clay minerals, such as carbonates, sulphates or sulphides. Therefore, in the thermal activation of the clays included in zone IV of the diagram must take into account the occurrence of potentially negative processes and the calcination strategy must be designed accordingly.

As an example of application of the proposed methodology, position of several clay samples are included in Fig. 1, including three high grade samples of Kaolinite (KW), Illite (IW) and Montmorillonite (MW) that were used as reference patterns. As could be observed, for clays with kaolinite content higher than 40% there is an almost linear correlation between content of  $Al_2O_3$  and LOI in the 350–850 °C temperature range, with the noticeable exceptions of samples with relatively high content of CaO (samples F and YG), where LOI are also related to decomposition of carbonate like minerals.

### 3 Conclusion

Selection criteria based on chemical composition ( $\%Al_2O_3 > 18$ ;  $Al_2O_3/SiO_2 > 0,3$ ;  $LOI > 7,0$ ; low  $\% CaO$  and  $SO_3$ ), allows a rapid screening of suitable clay deposits on a given area.

Correlation of weight loss with  $\%Al_2O_3$  allows a rapid assessment of the potentialities of clay deposits as a source of raw materials for the production of SCMs.

**Acknowledgments.** The authors would like to acknowledge the financial support of the Low Carbon Cement project, from SDC. They would also like to acknowledge to the Cuban Geological Services for the technical support in clay and limestone deposits sampling.

### References

1. Velde, B. (ed.): *Origin and Mineralogy of Clays. Clays and the Environment*. Springer Science & Business Media, Heidelberg (2013)
2. Chandrasekhar, S., Ramaswamy, S.: Influence of mineral impurities on the properties of kaolin and its thermally treated products. *Appl. Clay Sci.* **21**, 133–142 (2002). doi:[10.1016/S0169-1317\(01\)00083-7](https://doi.org/10.1016/S0169-1317(01)00083-7)
3. Murray, H.: *Industrial Clays Case Study*, IIED and WBCSD. MMSD-Indiana University (2002)
4. He, C., Osbaeck, B., Makovicky, E.: Pozzolanic reactions of six principal clay minerals: activation, reactivity assessments and technological effects. *Cem. Concr. Res.* **25**, 1691–1702 (1995). doi:[10.1016/0008-8846\(95\)00165-4](https://doi.org/10.1016/0008-8846(95)00165-4)

5. Fernandez, R., Martirena, F., Scrivener, K.L.: The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite. *Cem. Concr. Res.* **41**, 113–122 (2011). doi:[10.1016/j.cemconres.2010.09.013](https://doi.org/10.1016/j.cemconres.2010.09.013)
6. Fernández, R.: *Calcined Clayey Soils as a Potential Replacement for Cement in Developing Countries*, École Polytechnique Federale de Lausanne (2009)
7. Alujas, A.: *Obtención de un material puzolánico de alta reactividad a partir de la activación térmica de una fracción arcillosa multicomponente*, Tesis Doctoral, Universidad Central «Marta Abreu» de las Villas (2010)
8. Földvári, M.: *Handbook of Thermogravimetric System of Minerals and Its Use in Geological Practice* (2011)
9. Lemma, R., Irassar, E.F., Rahhal, V.: Calcined illitic clays as Portland cement replacements. In: Scrivener, K., Favier, A. (eds.) *Calcined Clays for Sustainable Concrete*, vol. 10, pp. 269–276. Springer, Dordrecht (2015). doi:[10.1007/978-94-017-9939-3\\_33](https://doi.org/10.1007/978-94-017-9939-3_33)
10. Lemma, R., Trezza, M., Rahhal, V.F., Irassar, E.F.: Thermal transformation of illitic - chlorite clays and its pozzolanic activity. In: VI Internacional Symposium of Chemistry, Facultad de Química-Farmacía, Universidad Central «Marta Abreu» de Las Villas (UCLV) Cuba, Cayo Santa María, Santa Clara, Cuba (2016)