Journal of Mining and Metallurgy, 41 A (2005) 1 - 9

EFFECT OF DIFFERENT DRY GRINDING PROCEDURES ON THE IMMERSION HEAT OF TALC AND CHLORITE

Jacques YVON[*], Frédéric VILLIERAS and Laurent MICHOT.

LEM, Laboratoire Environnement-Minéralurgie, UMR CNRS INPL-ENSG 7569.
15 avenue du Charmois 54 500 Vand?uvre - les - Nancy.
BP 40, 54 501 Vand?uvre - les - Nancy Cedex. Tel : xx 33 3 83 59 62 93.

(Received 12 June 2005; accepted 14 November 2005)

Abstract

Under dry grinding procedures, the immersion heat of the unit surface of talc stays as a constant close to 0.2 J/m^2 and reveals a weak hydrophilic behaviour. Chlorite crude mineral is more hydrophilic than talc, mainly due to inter-layered swelling sheets, but when ground it behaves according to two different mechanisms, leading to a strong decrease of the immersion heat. One mechanism involves the production of external surface with an immersion heat close to 0,23 j/m^2 that does not significantly differ from the talc one but dilutes the internal surface contribution. An other mechanism, involved in the early stages of comminution, could be the collapse of the internal surface due to mechanical effects, this collapse disappear when fineness increases, due to mechanical relax. The main conclusion is that the apparent hydrophilic behaviour of the crude chlorite mineral is mainly due to foreign swelling sheets with an average cross section area of 16Å^2 per exchangeable site, and decreases when grinding, up to reach the talc behaviour.

Key words: *Talc, chlorite, Clinochlore, fine grinding, dry grinding, immersion heat.*

[#] **Corresponding author:** *jacque.yvon@ensg.inpl-nancy.fr*

1. Introduction

Talc is a trioctahedral three layered sheet-silicate widely used under a finely divided state, in diverse applications (Garin & Yvon, 1995). Commonly talc is associated with trioctahedral chlorites, a four layered sheet-silicate. Though both the minerals can often be used together, some applications need either a selective out put or a separation process to reach purified talqueous or chloriteous grades, due to intrinsic differences in mineral properties ; talc is white and "hydrophobic", chlorite is weakly coloured and "hydrophilic" (Houot et al., 1993 ; Mailhac et al., 1985 ; Villieras et al., 1993a ; Yvon et al., 2002). Usually the talc and chlorite powders are submitted to subsequent grinding operations in controlled conditions (Michot et al., 1993) and, in some cases, to surface (Delon et al., 1995) or thermal (Villieras et al., 1993b) treatments that provide the final properties specific for each use.

Fine grinding is commonly used for shape and size monitoring but leads to significant alterations of non morphological properties of solids, it specifically affects the structural and surface properties and thus the behaviour of minerals in technical applications. This paper aims at describing the variation of some surface properties of talc and chlorite as a function of the dry grinding intensity.

2. Materials and methods

Talc-rich and chlorite-rich samples were collected in the Trimouns quarry that provides a metasomatic ore (Moine et al., 1982). Samples were crushed, homogenised and quartered into subsamples, the subsamples were dry ground in different ways without classification according to the flowsheet descibed by Yvon et al., (1987, 1995).

Two laboratoty mills have been used, one is a fix hammer mill (Forplex 00) the second is a bowl and ring mill (AUREC T 100). T0 and C0 are, respectively, crude talc-rich and chlorite-rich samples. TnF is the talc-rich sample ground n times in the FORPLEX mill, CnF is the chlorite-rich sample ground n times in the FORPLEX mill, TmS is the talc-rich sample ground m seconds in the AUREC mill, CmS is the chlorite-rich sample ground m seconds in the AUREC mill.

The present talc mineral has a composition very close to its theoretical definition: $Mg_{2,97}Fe_{0,03}Si_4O_{10}(OH)_2$. The Present chlorite is a clinochlore derived from the alteration of pegmatite, its schematic structural formula is $Mg_{4,78}Fe_{0,12}Al_{1,1}(Si_{2,9}Al_{1,1})O_{10}(OH)_8$. (Yvon et al., 1995). Since the ore does not provides enough pure talc and chlorite easy to sort, the grinding tests have been carried out on impure samples and the properties of pure minerals calculated according to the method developed by Yvon et al., (1987, 1995).

The specific surfaces were determined using conventional step by step low temperature nitrogen adsorption isotherms. The particle size distributions were determined using the Sedigraph 5000D device. The morphological parameters were deduced from particle size distributions and specific surfaces according to the method developed by Cases et al., (1986). The Cationic Exchange Capacities (CEC) were determined using a potentiometric titration method The immersion heats were measured Using a Setaram MS 70 micro-calorimeter, without precoverage, after outgazing 12 h, at 105°C, under a 10^{-3} torr. residual pressure, according to the procedure and formalism described by Yvon et al., (1994); the immersion is carried on in water in equilibrium with the solid to avoid dissolution effects.

The immersion heat (Qim) can be written according to the following formula (Yvon et al., 1994).

$$Q_{im} = - (Na.\Delta H_{Vap} + \Sigma Na_{i.}H_{i\ Ads}) + A(\gamma - T.\delta\gamma/\delta T)$$

Where $\Delta Hi_{\ Ads}$ are the adsorption enthalpies of the Nai water vapour molecules, with $\Sigma Na_i = Na$, ΔH_{Vap} the vaporisation enthalpy of water, A the water/vapour surface to be suppressed during immersion, γ the liquid vapour surface tension of water and T the temperature. Though the immersion heat is a complex phenomenon, it can be noticed that the term $(\gamma - T.\delta\gamma/\delta T)$ is equal to 119,5 $mj.m^{-2}$ for water at 30°C, then any excess compared to this value denotes an hydrophillic behaviour.

3. Background

It has been previously established, on the same materials, the following data, derived from the variations of Cationic Exchange Capacities

(CEC) (Yvon et al., 1987)… The CEC of talc only results from the dissociation of silanol groups on its lateral surface where the cross section area of each exchangeable site is 19,5Å^2. The CEC of the present chlorite has three different origins: 1) a structural CEC of about 5,8 meq/100g, 2) a CEC resulting from Si-OH and Al-OH groups dissociation on lateral surface with a cross section area of 29,5Å^2, and 3) a CEC resulting from the hydroxide sheet leaching. One half of the Mg is leached off a basal face if it consists of a hydroxide sheet and the contribution of Mg leaching from the hydroxide layer on the lateral surfaces generates a CEC three times that of the tetrahedral border CEC.

In addition, it has been demonstrated (Michot et al., 1994) That the macroscopic hydrophobicity of talc results from the interaction of the OH structural groups of the basal surfaces with nitrogen and that talc, when outgazed in severe conditions, becomes hydrophilic and stays hydrophilic when nitrogen is replaced by water.

Finally the surface of talc accessible to water can be considered as an external one with two components, on lateral and the other basal, with a ratio lateral/basal close to 0,1. The surface of chlorite can be considered to have an external component with a ratio lateral/basal close to 0,15, but with in addition, an internal surface corresponding to water accessible non-equilibrated sheets (Swelling sheets), since it can be titrated by potentiometric methods.

4. Results and discussion

Specific surfaces and immersion heats of pure minerals are reported in table 1. The variations of immersion heat in equilibrated solutions are reported in fig 1 as a function of the specific surface.

First of all it must be noticed that the immersion heat in distilled water every time exceeds that in equilibrated solutions, what means that the contribution of dissolution terms strongly affects the immersion heat, this observation explains the well known formation of nesquehonite in air dried talc slurries (Michot 1990). The immersion of talc in an equilibrated solution is close to 0,2 J/m^2, then talc is a weakly hydrophilic compound in the present outgazing conditions (at 30°C, the adhesion work of water against water, i.e.

the contribution of the surface is 0,12 mj/m^2). The immersion heat per unit area does not depend on fineness neither on the grinding procedure.

Table 1. Specific surfaces and immersion heats of pure minerals after different grindings.

Sample code	Specific surface m^2/g	Immersion heat distilled water J/m^2	Immersion heat equilibrated solution J/m^2	Sample code	Specific surface m^2/g	Immersion heat distilled water J/m^2	Immersion heat equilibrated solution J/m^2
T0	1,6	0,368	0,216	C0	2,5	1,086	0,749
T1F	1,8	0,315	0,213	C1F	2,7	1,006	0,606
T2F	1,8	0,296	0,230	C2F	2,6	0,898	0,704
T3F	2,5	0,224	0,158	C3F	2,8	0,886	0,552
T4F	2,4	0,222	0,205	C4F	3,0	0,964	0,394
T5F	2,4	0,345	0,140	C5F	3,1	1,164	0,613
T5S	2,6	0,274	0,184	C5S	3,2	0,868	0,208
T10S	3,2	0,234	0,224	C10S	4,6	0,651	0,242
T20S	4,0	0,268	0,240	C20S	4,2	0,771	0,405
T40S	7,3	0,234	0,160	C40S	5,2	0,781	0,484
T80S	8,6	0,349	0,181	C80S	7,9	0,712	0,388
T120S	13,0	0,461	0,220	C120S	9,8	0,766	0,363

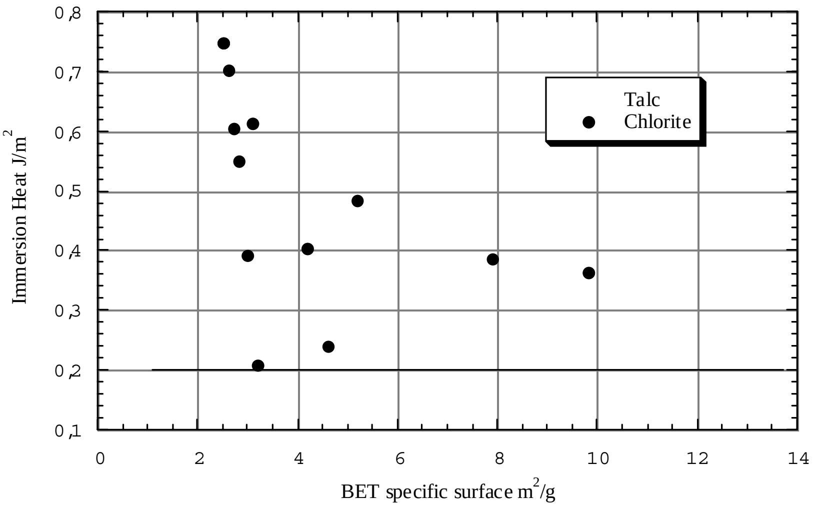

Fig. 1. Variation of the immersion heats in equilibrated solutions of pure minerals as a function of the BET nitrogen specific surfaces.

The immersion heat of unground chlorite is greater than that of talc and reveals the more hydrophilic macroscopic behaviour of this mineral (Figure 1).

However when the grinding intensity increases, the immersion heat of chlorite decreases according to two distinct mechanisms (figure 1). The immersion heat of chlorite drastically decreases with a minimum for specific surfaces ranging between 3 and 4;5 m^2/g; in this domain, the immersion heat of chlorite reaches the immersion heat of talc. For finer granularities, the immersion heat increases and stabilises on a decreasing hyperbolic branch.

The hyperbolic decrease of chlorite is easy to understand considering that grinding increases the external surface accessible for nitrogen and water, but cannot change the internal one only accessible for water. Then this behaviour can be interpreted as a dilution of a constant internal surface "a" by an increasing external surface "SS" and modelled according to the following formula.

$$Q_{im} = k(a + SS)/SS$$

where "Qim" is the observed immersion heat and "k" the immersion heat of the unit area "a" the internal surface area and "SS" the BET nitrogen surface area. Applying this model to the upper limit of figure 1 leads to

$$k = 0{,}23\ j/m^2 \text{ and } a = 5{,}6\ m^2/g.$$

According to these determinations, it can be stated that the external surface of the chlorite mineral is only slightly more hydrophilic than the talc one. It can also be easily calculated that the internal surface contains one exchangeable site each 16$Å^2$. Considering that a vermiculite half unit cell can be written as

$$(Al(_{2-x})M^{2+}{}_{x})(Si(^{4-y})M^{3+}{}_{y})O_{10}\,(OH)_2\ \ (x+y)/n.Cat^{n+}$$

and that the unit cell has roughly a surface of 50$Å^2$, then the sum (x+y) is equal to 1,56 this value is compatible with a high charge swelling sheet as vermiculite one.

Concerning the early decrease and the minimum observed between 3 and 4,5 m^2/g, one hypothesis can be that mecano-chemical effects lead to a collapse of the internal surface stabilised by non relaxed elastic constraints that finally relax when the grinding intensity exceeds a threshold value. Such an hypothesis supposes that the swelling sheets responsible for the structural CEC are not completely continuous in the chlorite structure, or are made non accessible by grinding.

Though the collapse of swelling sheets would have to decrease the apparent CEC, this effect is suppressed by the fact that the decationizing treatment has a dispersing action and opens the collapsed layers.

5. Conclusions

Crude chlorite is really more hydrophilic than crude talc due to structural properties, but fine grinding produces on the chlorite a surface the characteristics of which are close to those of talc. Therefore, one can expect similar behaviours of finely dry ground talc and chlorite either in separation process or in technical applications involving contrasts in hydrophilic-hydrophobic balance. Paying account of the immersion experiments, one can assume that finely dry ground chlorite is not really more hydrophilic than finely dry ground talc.

6. Acknowledgements

Thanks are due to "Délégation Générale ? la Recherche Scientifique et Technique" AC VRSS Grant 78-07-0749, and to the company "Talc de Luzenac SA".

7. References

1. J.M. Cases, P. Cunin, C. Poinsignon & J.Yvon, (1986), Methods of analysing morphology of kaolinite: relations between crystallographic and morphological properties. Clay Minerals. 21, (1), pp. 55-68.

2. J.F. Delon, J.Yvon, L.Michot, F. Villieras & J.M. Cases, (1995), Vapour phase adsorption of alkylamines on talc and chlorite. Actes

Eurofillers'95 Mulhouse 11-14 sept. MOFFIS and FILPLAS eds. pp. 17-20.

3. P. Garin & J.Yvon, (1995), Les charges et pigments minéraux. Sciences Géologiques, 46, (1-4), pp. 267-280.

4. R. Houot, R.Joussemet & S. Yang, (1993), Valorisation par flottation et séparation magnétique des talcs pyrénéens. Revue de l'Industrie Minérale, Mines et Carri?res. Les techniques. 75, pp. 56-61.

5. J. Mailhac, B.Gavoille & P. Cunin, (1985), Le tri optique aux Talcs de Luzenac. Revue de l'Industrie Minérale. Les techniques. 85, pp. 269-276.

6. L. Michot, (1990). Propriétés physico-chimiques superficielles du talc et de la chlorite. PhD thesis INPL Nancy, 285

7. Villiéras F., J. Yvon & G. Fourty, (1993), Multistage wet grinding of talc Relation between physicochemical parameters of the filler and mechanical properties of filled polypropylenes. Journal of Materials Science. 28, pp. 1856-1866.

8. L.J. Michot, F. Villiéras, M. François, J. Yvon, R. Le Dred & J. M. Cases, (1994), The structural microscopic hydrophilicity of talc. Langmuir. 10, pp. 3765-3773.

9. B. Moine, B. Gavoille & J. Thiébaut, (1982), Géochimie des transformations métasomatiques ? l'origine du gisement de talc et de chlorite de Trimouns (Luzenac, Ari?ge, France)I. Mobilité des éléments et zonalités . Bulletin de Minéralogie, 105, pp. 62-75.

10. F. Villiéras, S. Montes, J. Yvon,. & J.M. Cases, (1993a),Valorisation directe des talcs pyrénéens. Revue de l'Industrie Minérale, Les techniques IV-V/ 93. Mines et Carri?res, 75, pp. 37-40.

11. F. Villiéras, J. Yvon, M. François, J.M. Cases, F. Lhote, J.P. Uriot, (1993b), Micropore formation due to thermal decomposition of hydroxide layer of Mg-chlorite: interactions with water. Applied Clay Science. 8, pp. 147-168.

12. J. Yvon, J.M. Cases, R. Mercier & J.F. Delon,(1987), Effect of comminution on the cation exchange capacity of talc and chlorite from Trimouns, France. Proc. VIIIth International Clay Conf. The Clay Mineral Society. L.G. Schultz, H. Van Olphen and F.A. Mumpton eds. Bloomington, IN. pp. 257-260.

13. J.Yvon, F. Thomas, F. Villieras & L.J.Michot, (1994), Surface - Activity of water. In "Powder technology and Pharmaceutical Process".

Handbook of powder technology Vol 9. D. Chulia, Y. Pourcelot and M. Deleuil eds. Elsevier Science publishers B.V. Amsterdam. chap IV, pp. 79-113.

14. J. Yvon, L. Michot, F. Villiéras & J.M.Cases, (1995),Differential dry grinding of talc and chlorite, consequence for air classification separation. Actes Eurofillers'95, Mulhouse 11-14 sept. MOFFIS and FILPLAS eds.13-16.

15. J. Yvon, J.M. Cases, F. Villiéras, L. Michot & Thomas F. (2002). Les minéraux techniques naturels: connaissance, typologie et propriétés d'usage. C.R. Ac Sc. Géoscience, 334, pp.717-730.