

# **Polyol-type Compounds as Clinker Grinding Aids: Influence on Powder Fluidity and on Cement Hydration**

C. Jolicoeur<sup>2</sup> S. Morasse<sup>1</sup>, J. Sharman<sup>2</sup>, A. Tagnit-Hamou<sup>2</sup>, F. Slim<sup>3</sup>,  
M. Pagé<sup>4</sup>

<sup>1</sup>*Norampac Inc, Toronto, Canada;* <sup>2</sup>*Université de Sherbrooke, Sherbrooke, Canada;* <sup>3</sup>*Ciment Québec, St-Basile, Canada;* <sup>4</sup>*Handy Chemicals, Candiac, Canada*

## **ABSTRACT**

A series of polyol compounds was investigated to establish the potential usefulness of these materials as cement grinding additives. Measurement of the cement powder fluidity induced by these compounds showed that very substantial fluidity improvements can be achieved with low molecular weight 1,2-diols, the effect being strongly dependent on the aliphatic groups of the diol molecules. Such molecules can thus promote the dispersion of cement particles, as required to improve the efficiency of clinker grinding processes. From calorimetric measurements of the heat of cement hydration, the polyols tested were also shown to exert a moderate acceleration of the hydration reactions. Hence, selected polyol-type compounds can be useful in cement grinding aid formulations which simultaneously aim to improve grinding efficiency and control cement hydration behaviour.

## **1. INTRODUCTION**

Organic additives are widely used as 'grinding aids' in a variety of dry or wet mineral milling operations. In the Portland cement industry, the functions of the grinding aid are to 1) reduce the energy required to grind the clinker to a given fineness; and 2) increase the throughput of a grinding mill at constant energy [1,2]. These objectives can usually be achieved with relatively small quantities of the organic additive, typically less than 0.1%. Even at such low dosages, however, grinding aids can have important effects on the properties of the cement produced: powder fluidity; rheological properties of fresh cement pastes; and the course of cement hydration reactions [1,3-4].

In one aspect of the mode of action of grinding aids, it is widely recognized that such additives increase the dispersion and the flowability of the cement powder. This markedly facilitates the extraction of the finely ground particles (fines) from the mass, thus reducing the amount of

material which is re-circulated into the mill and, therefore, increasing the ratio of impacts that effectively increase the surface area [1,2]. The increased powder fluidity is also highly beneficial for handling and transportation of the cement powder; this fluidity is readily evaluated through the 'packset' test.

On the other hand, the various additives that compose a grinding aid formulation may have significant effects on cement hydration and on the rheology of cement pastes or concrete. Some formulations contain dispersants, which decrease water demand, while other additives may produce the opposite effect [2]. The grinding additives may also interact with the cement hydration reactions, either retarding or accelerating these processes. Clearly, such effects must be considered when designing grinding aid formulations [2-4].

This paper investigates the effect of various polyols, used as grinding additives, on selected properties of cement. The polyols investigated include ethylene glycol, propylene glycol and several derivatives or analogues of these glycols [1].

## 2. EXPERIMENTAL

### 2.1 Materials

The cement used in this study was a GU (CSA Type 10) cement that had been ground without any grinding aids; the composition of the clinker used to make this cement is shown in Table 1. While grinding experiments were performed in the presence of selected polyols, it was found more reliable to start with a cement powder obtained without any grinding aid, and then blend in the additives of interest to achieve a surface coating of the particles. In this way, it is possible to determine the influence of the various additives at constant cement fineness. The additives used were neat liquids and are listed in Table 2.

**Table 1: Clinker composition.**

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>	Alkali	Free CaO
20.4	5.5	3.6	63.9	2.4	1.3	1.0	0.6

### 2.2 Methods

The various additives tested were blended with the cement at dosages ranging between 0.015 and 0.15 wt%, using a high energy attritor under the following conditions: 1375 g steel balls (d=6.6mm), 500 g cement, 85°C, 300 rpm, t = 5 minutes. This procedure provided an adequate and reproducible homogenization with the least impact on particle size.

**Table 2: Name and abbreviation of the grinding aids used.**

Abbreviation	Name	Abbreviation	Name
TEA	Triethanolamine		
EG	Ethylene glycol	PG	Propylene glycol
DEG	Diethylene glycol	DPG	Dipropylene glycol
TEG	Triethylene glycol	TPG	Tripropylene glycol
PEG	Poly(ethylene glycol)	PPG	Poly(propylene glycol)
12HD	1,2-Hexanediol	12OD	1,2-Octanediol
12BD	1,2-Butanediol	23BD	2,3-Butanediol
GLY	Glycerol	PPT	Polypropylene glycol triol
MPdiol	2-methyl-1,3-propanediol	DMPD	2,2-dimethyl-1,3-propanediol
LF2	Mixed EG-PG copolymer	LG650	Polypropylene glycol triol

Following the cement-additive blending, 200 g of sample was sieved on a 63µm vibrating sieve as a function of time in order to evaluate the powder fluidity. A fluidity index was then calculated as:

$$\frac{P}{P_{\max}} = \frac{bt}{1+bt} \quad \text{or} \quad \frac{t}{P} = \frac{1}{bP_{\max}} + \frac{t}{P_{\max}} \quad (1)$$

where P is the amount of cement passing through the sieve at time t, P<sub>max</sub> is the maximal amount passing, and b is the fluidity index [1].

The cement hydration reactions were monitored by recording the heat evolved from cement paste samples in an isoperibol calorimeter. In the latter, the sample cell is surrounded by a water bath, which is actively maintained at the same temperature as the sample, thus minimizing any heat exchange between the sample and the environment.

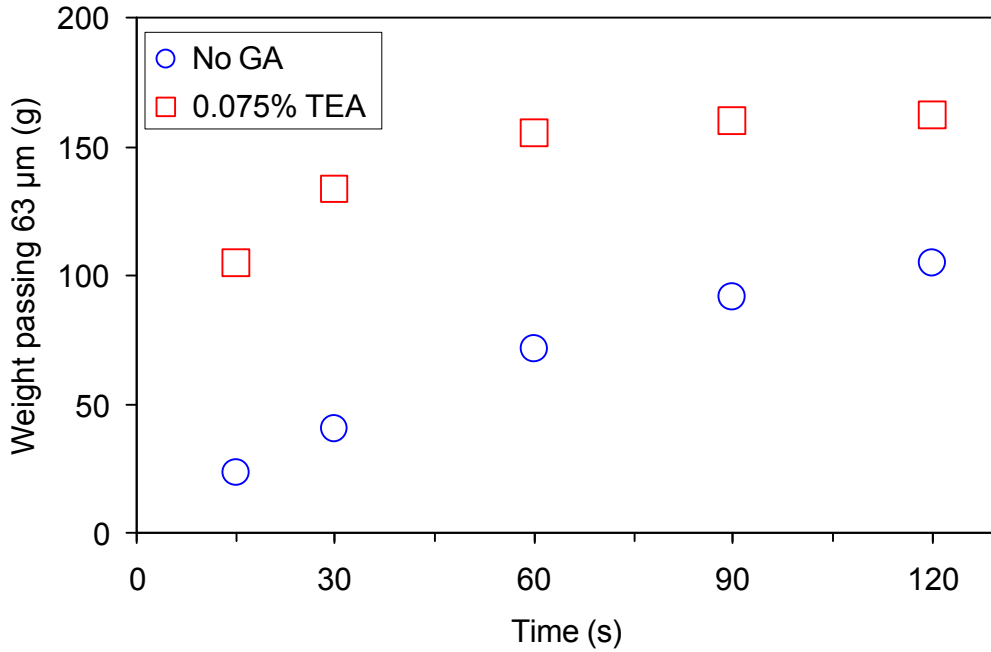
### 3. RESULTS

#### 3.1 Powder fluidity

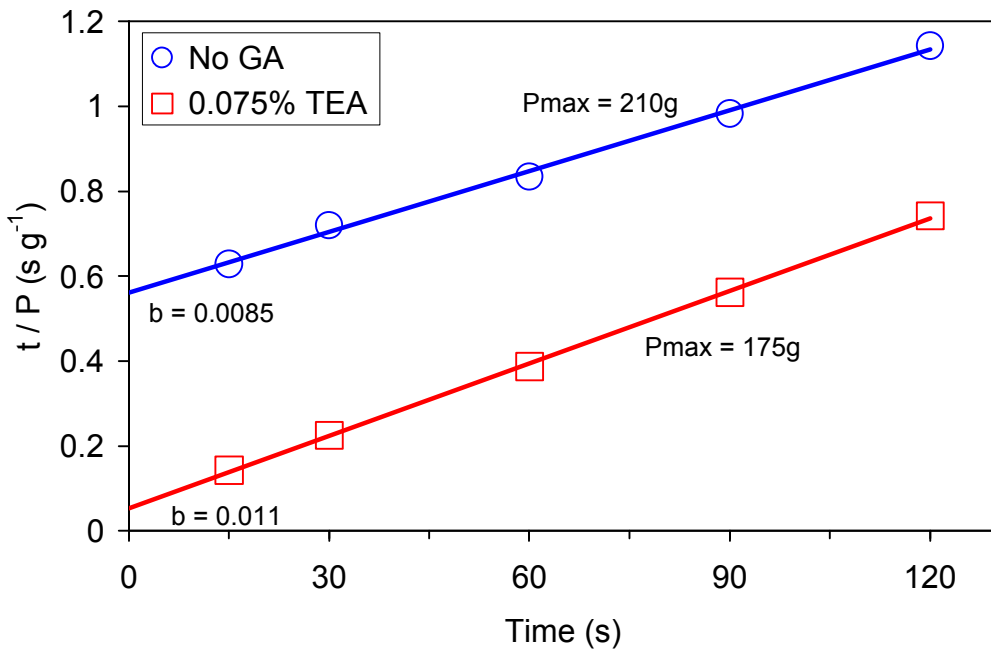
Various additives were intimately blended with the cement powder under conditions described above. Reference samples were obtained by mixing

the cement with triethanolamine, an ingredient commonly found in various commercial clinker grinding admixtures.

Figures 1 and 2 present the fluidity measurements as function of time for the untreated cement powder and of the cement blended with TEA; the first figure presents an example of the data collected: weight of material



**Figure 1: Effect of TEA on the fluidity of cement as determined by sieving.**

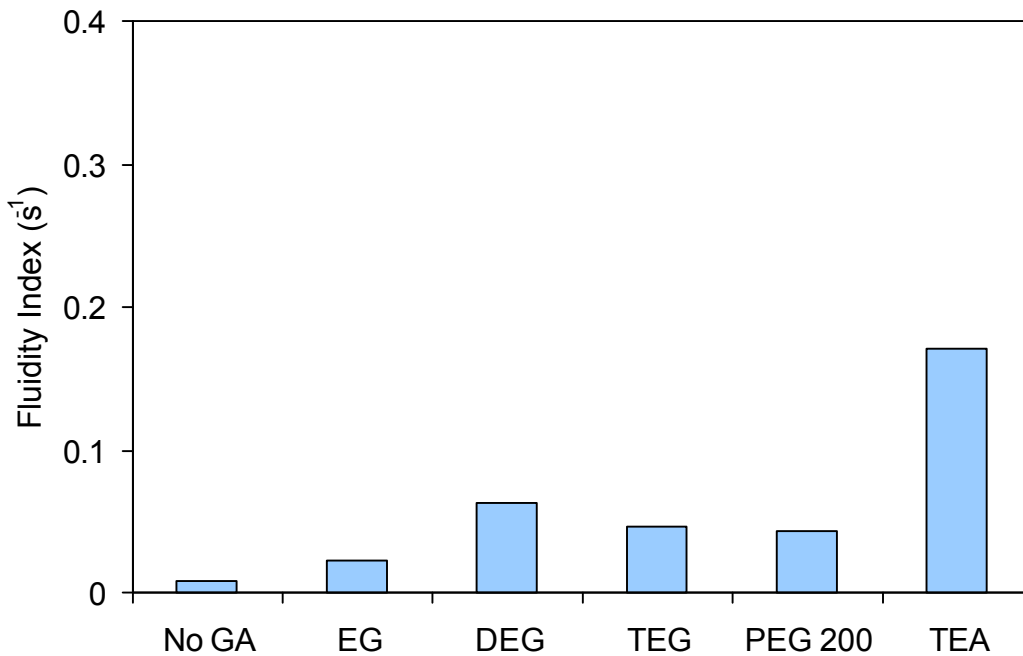


**Figure 2: Linearization of fluidity data to determine the fluidity index**

passing through the sieve over time, while the second figure represents the data fitted to equation 1. The latter plot is used to determine a 'fluidity index' (b) that was used to compare the dispersing ability of the various additives. As can be seen from these figures, TEA greatly increases the fluidity of the cement powder; in the presence of TEA (0.075%) the fluidity index increases from 0.009 for the cement alone to 0.11 for the TEA-treated cement.

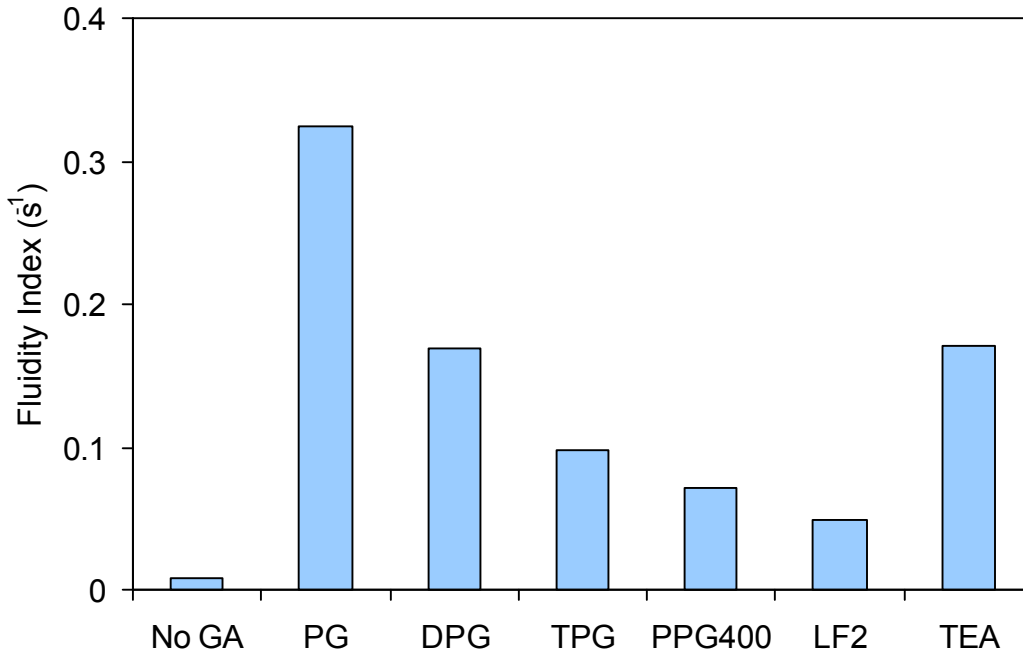
The first set of additives examined in this study comprises ethylene glycol (EG) and several oligomers of EG. These products have been demonstrated to promote grinding of cement clinker [6] and are also found in proposed grinding aid formulations [2-5]. The fluidity indices obtained with these products, at a dosage of 0.1wt%, are presented in Figure 3. The additives tested all demonstrate an increase in the powder fluidity with a maximum effect attained with the diethyleneglycol (DEG); however, none of these products achieves the fluidizing effect of TEA.

The second series of additives tested is derived from propylene glycol (PG). Fluidity results obtained with PG and its oligomers are illustrated in Figure 4, together with those for LF2, an EG-PG block copolymer. The PG derivatives demonstrate a greater fluidizing effect than the EG series. In this case, however, the maximum effect is observed with the monomer (PG); for the oligomers, the fluidity index decreases with increasing molecular weight. Only PG produced a greater fluidity than TEA, the dimer, DPG, giving results similar those obtained with TEA. The EG-PG co-polymer is not significantly better than the EG polymer (PEG200, Fig 3)

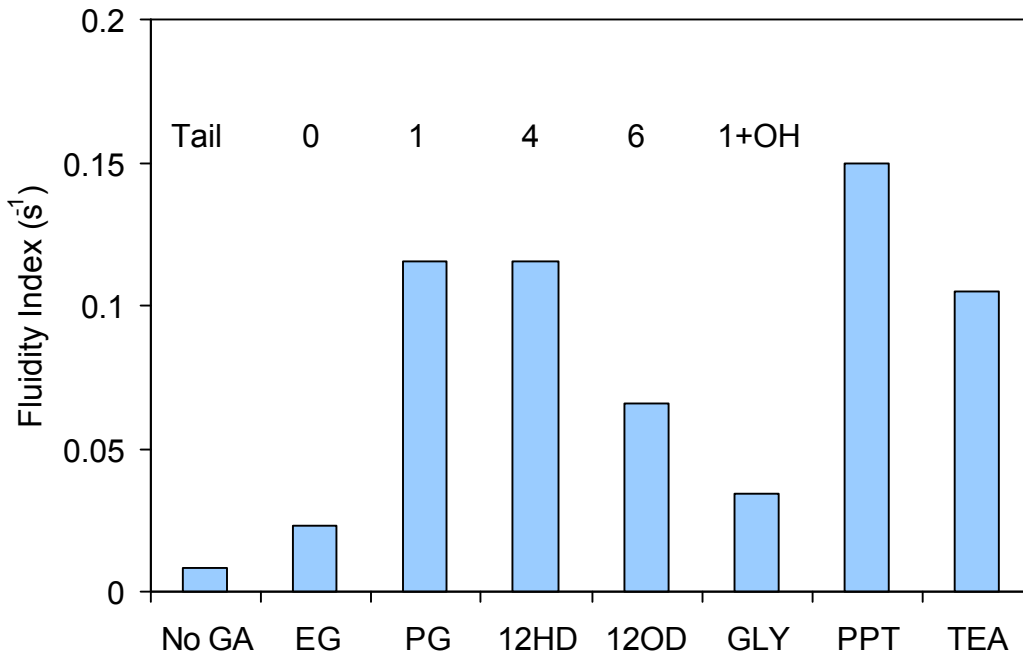


**Figure 3: Fluidity index obtained for the ethylene glycol series**

Based on the results for the EG and PG series, it was decided to compare products having analogous 1,2-diol structures: that is 1,2 ethanediol (EG), 1,2-propanediol (PG), 1,2-hexanediol (12HD) and 1,2-octanediol (12OD). These products have two adjacent alcohol groups and, with the exception of EG, all have an aliphatic tail. The effect of the size of this tail is illustrated in Figure 5, at a common dosage of 0.075%; from these data, it



**Figure 4: Fluidity index obtained for the propylene glycol series**



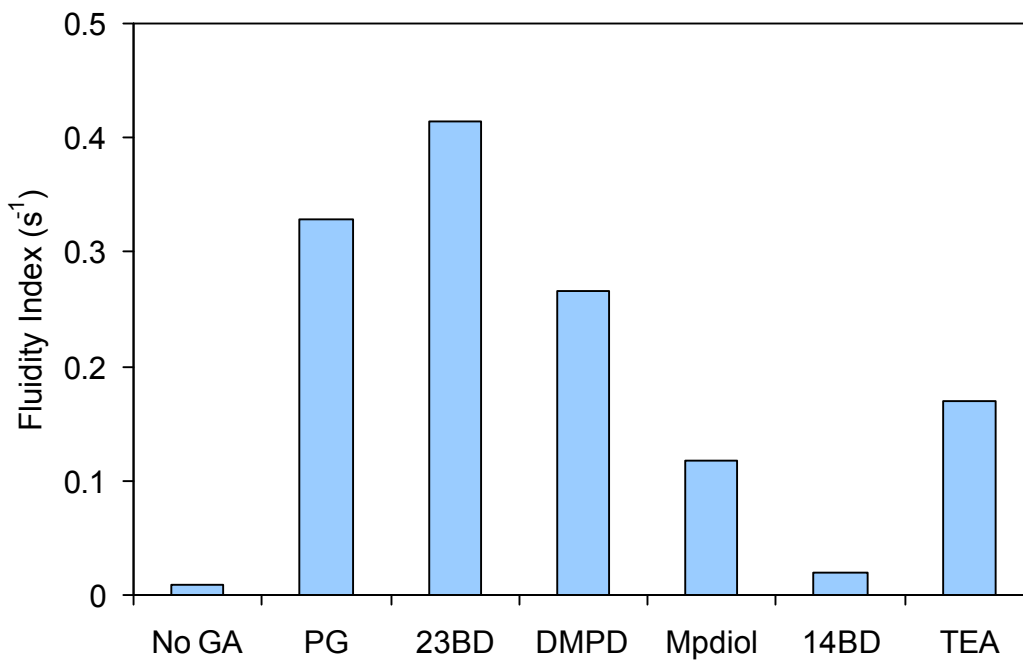
**Figure 5: Effect of tail length of propylene glycol analogues on the fluidity index (0.075% additive)**

is apparent that maximum fluidity is obtained with a 1,2-diol having a tail containing between 1 and 4 carbons (PG and 12HD). Both PG and 12HD produced a greater fluidity than TEA. Clearly, the presence of the aliphatic group on the diol plays an important role in particle-particle repulsion and powder fluidity.

Glycerol (GLY) was included with the 1,2-diol series in Fig 5 since its structure is related to that of PG, i.e., GLY is equivalent to PG with an additional hydroxyl group. Interestingly, GLY has a much lower fluidizing effect than PG. On the other hand, low molecular weight polymers derived from glycerol and propylene oxide (precursor of PG) (PPT) exhibit a good fluidizing effect, beyond that observed with PG. This is surprising in that polymerisation of PG itself appears to decrease its efficiency.

The fourth series of additives investigated in this study is related to butanediol. For these additives (tested at 0.1wt%), the fluidity index values reported in Figure 6, show that the molecular structure of the products butanediol and 2,3-butanediol, having the same chemical formula,  $C_4H_{10}O_2$ , both diols, produce widely differing effects depending on the relative position of their hydroxyl groups. The fluidizing effect of 23BD is 16 times greater than that of 14BD. In fact, 23BD is significantly more effective than PG or TEA, whereas 14BD produces the same effect as EG.

Another example of the important influence of molecular structure is demonstrated by the comparison of DMPD and MPdiol, i.e., 2,2-dimethyl 1,3-propanediol and 2-methyl 1,3-propanediol respectively. In this case,

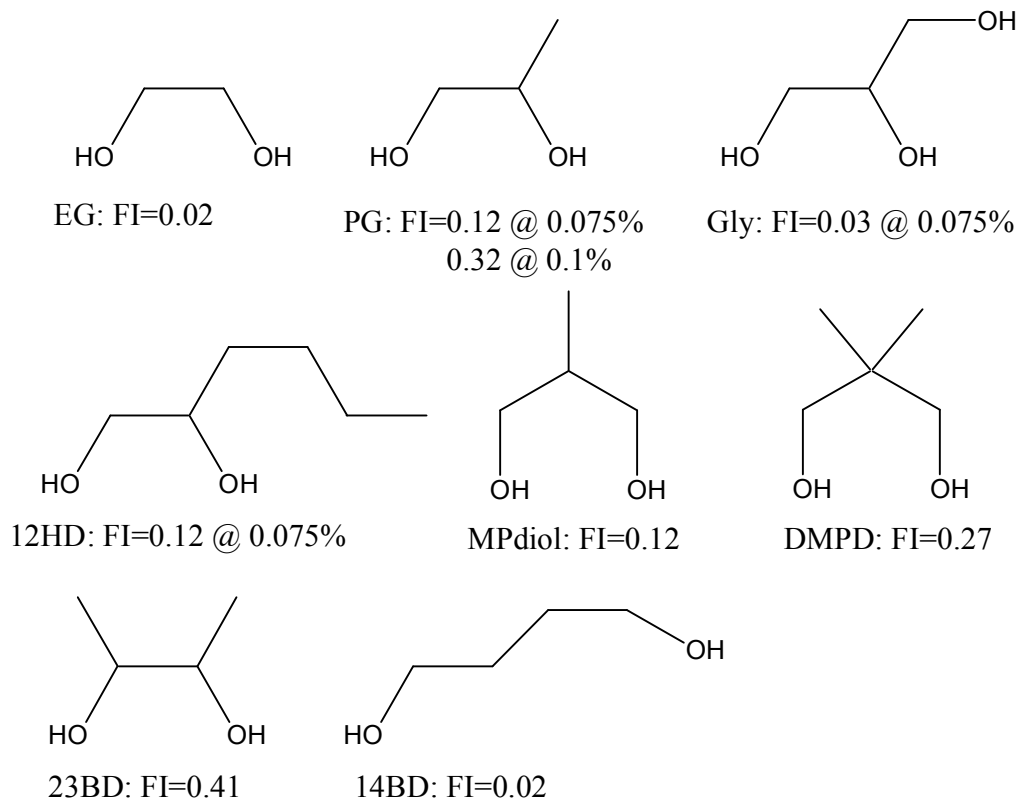


**Figure 6: Fluidity index obtained with butanediol and analogues**

the addition of a methyl group to MPdiol, which has a good fluidizing effect similar to TEA, doubles the fluidizing power of this molecule almost to the level of PG.

To visualize the relationship between molecular structure and the fluidizing ability of the additives, Figure 7 illustrates a representation of some of these structures, along with the observed fluidity indices at either 0.075 or 0.1wt%. Examination of these structures, in the light of the observations above, the following comments may be advanced:

- With molecules like EG and GLY, there is no hydrophobic tail and apparently little repulsion between the cement grains.
- With DEG and TEG, the hydrophilic nature is weakened somewhat, compared to EG, giving rise to an increase in the fluidity index.
- The addition of small hydrophobic tails, such as with PG, MPdiol and 23BD, would appear to increase the inter-particle repulsion giving rise to the observed increase in fluidity index.
- When the size of the hydrophobic tail becomes too important, the fluidity index drops. This may be due to an excessive hydrophobicity or to a lower vapour pressure of the molecules having a higher molecular weight; the latter would make it more difficult to achieve an even distribution of the additives over the surface of the cement grains.



**Figure 7: Molecular structure and fluidity index of selected GA (dosage = 0.1% unless otherwise noted).**



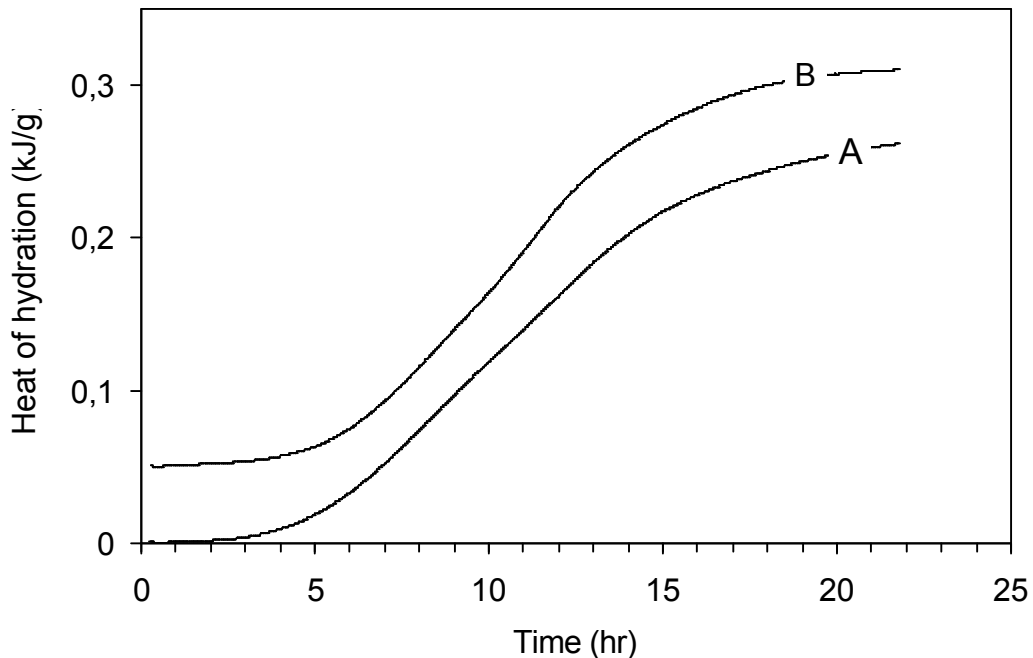
At this stage of the investigation, it can be concluded that the 1,2-diol functionality is adequate to ensure proper binding of the additives to the surface of the cement particles. The presence of an aliphatic chain attached to the diol structure enhances the fluidizing ability; however, the presence of two separate hydrophobic groups (such as the two methyl groups in 23BD) apparently provides an even better powder fluidification.

### 3.2 Cement hydration

As noted above, the various additives tested interact with the surface of the cement grains to modify the properties of the dry powder; it should therefore be expected that these additives could also influence cement hydration. Indeed previous studies, employing these products as either grinding aids or concrete admixtures, have evidenced effects on cement hydration and on the rheology of cementitious mixtures [3-6]. This part of the study examines the influence of the various additives on the cement hydration rates through heat of reaction measurements.

The samples used in hydration studies were prepared, as described above for fluidity measurements. Cement pastes were prepared with a w/c of 0.45 and the sample temperature was equilibrated to 25°C prior to inserting the sample into the calorimeter after 10-15 min of initial hydration.

Figures 8 and 9 present typical heat and heat flow curves respectively for cement with and without 0.1% TEA (TEA data has been shifted to facilitate

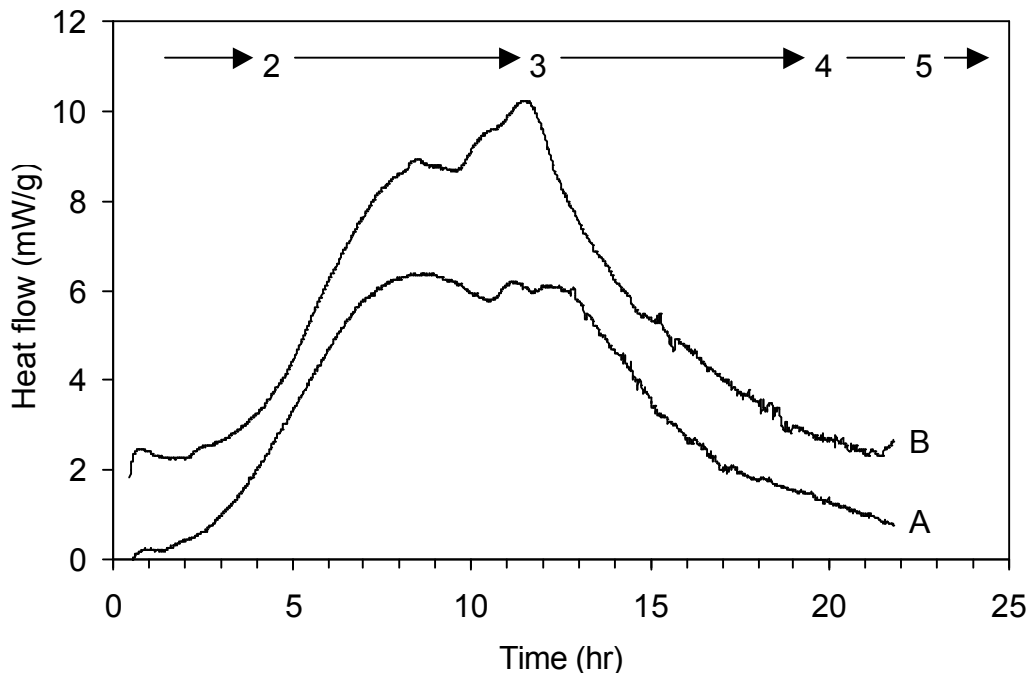


**Figure 8: Thermograms of cement pastes made from cement mixed with (B) and without (A) 0.1% TEA, w/c 0.45**

comparison). Although some differences are noticed in the heat curves (Fig 8), these become more apparent in the derivative heat flow curves (Fig 9). The latter also allows separation of the curves into the usual 5 periods: (1) pre-induction period where readily soluble products enter into solution and initial  $C_3A$  and  $C_3S$  reactions occur; (1-2) induction or dormant period where little activity is observed; (2-3) acceleration period where setting occurs; (3-4) deceleration and (5) ageing periods where hardening and strength gain occur. The first and principal peak that is observed reflects the beginning of the acceleration period and is attributed to hydration of  $C_3S$ ; the second peak is attributed to hydration of the aluminate phases.

Any important effects of the additives on the hydration rates should be detectable in the heat flow curves, i.e, accelerators will shorten the induction period, while retarders will lengthen it, etc... In the presence of 0.1% TEA, there is no marked change in the duration of the induction period; similarly, the two hydration peaks occur at roughly the same time, with or w/o TEA, although the second peak appears to be sharper in the presence of TEA. To allow further, more detailed comparisons, the heat data for cement alone was subtracted from the data obtained with cement in the presence of the various additives. This yields differential thermograms, which evidence minute differences in the heat curves.

The differential curves obtained with various dosages of TEA are presented in Figure 10. In the latter, it is readily apparent that while TEA

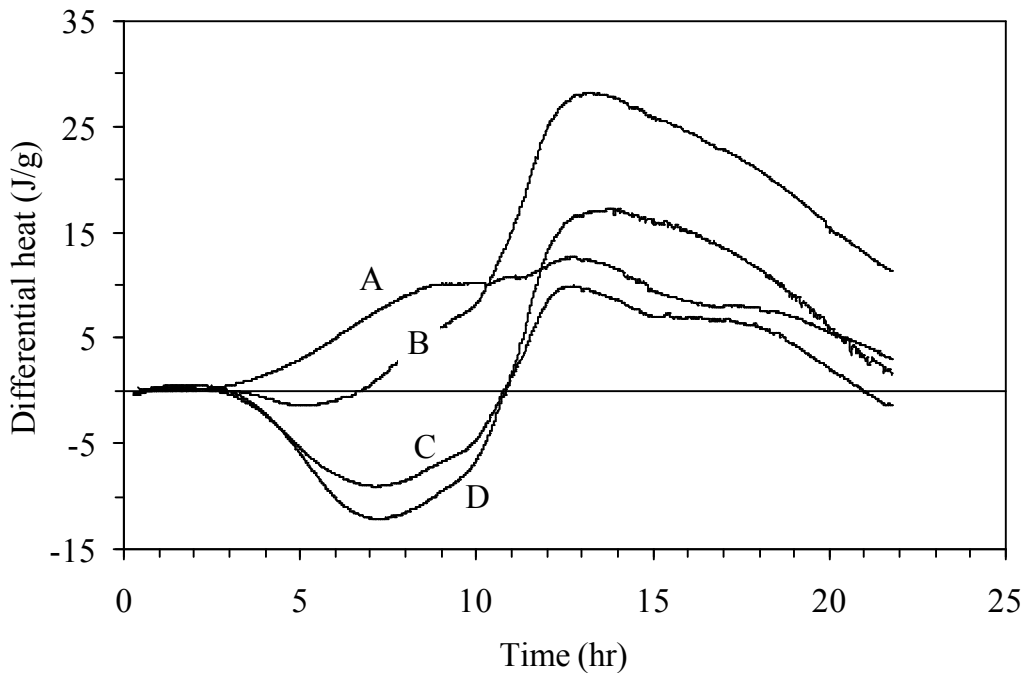


**Figure 9: Heat flow curves of cement pastes made from cement mixed with (B) and without (A) 0.1% TEA, w/c 0.45.**

does not affect the length of the induction period, it greatly affects the rates of reaction for both  $C_3S$  and the aluminate phases. At very low dosages, 0.015%, TEA acts as an accelerator for  $C_3S$  while at higher dosages it acts as a retarder. On the other hand, TEA is seen to accelerate the reaction of the aluminate phases passing through a maximum between 0.075 and 0.1%.

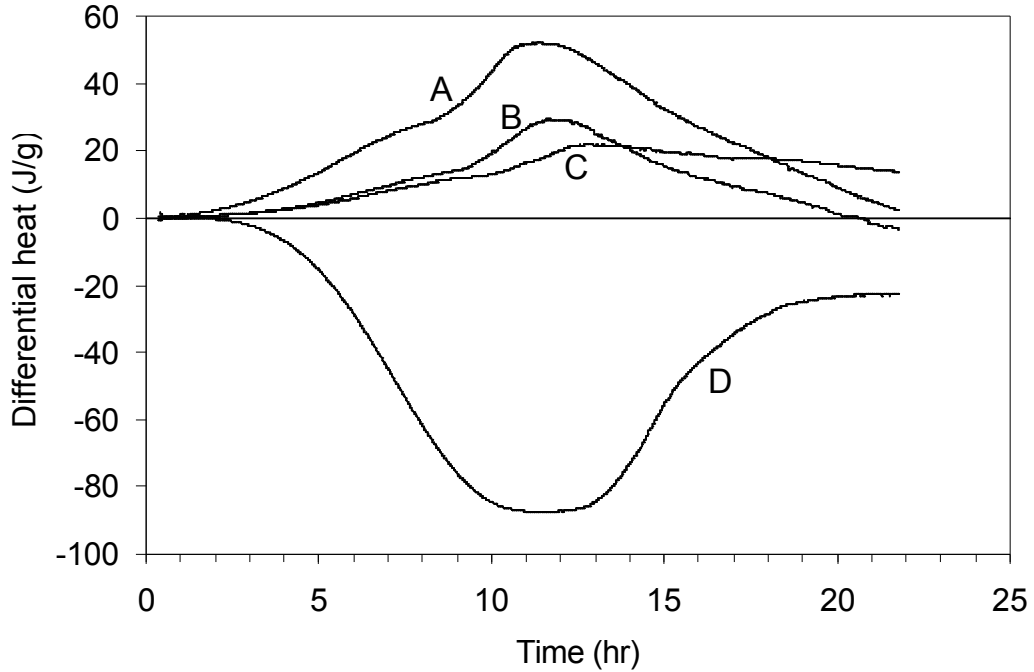
The effect of various polyols on cement hydration rate is presented in Figure 11, again from difference thermograms. From these data, it is readily apparent that these additives also exert important effects on hydration. Glucose has been added to this series to demonstrate the effect of a known retarder; at 0.075%, glucose greatly retards  $C_3S$  hydration and also appears to retard that of the aluminate phases. Glycerol and LG650, a polypropylene oxide derivative of glycerol similar to PPT, on the other hand, both accelerate  $C_3S$  and aluminate hydration at this dosage. GLY apparently accelerates cement hydration more than does TEA; it also appears to shorten the induction period.

Although tested at a slightly different dosage compared to the other polyols, PG accelerates the hydration of both the silicate and aluminate phases, though not to the same extent as GLY or LG650. However, the accelerating (promoting) influence of PG remains for nearly 24 hrs. This is reflected in the total heat of hydration measured over the 22 hr experiment as reported in Table 3. According to these data, the total heat is not



**Figure 10: Difference thermograms of cement mixed with various TEA dosages: A: 0.015%, B: 0.075%, C: 0.1% and D: 0.15% TEA.**

significantly affected by GLY and LG560, but it is increased in the presence of PG, the effect is comparable to that of TEA at intermediate concentrations.



**Figure 11: Influence of various polyols on the difference thermograms for cement hydration: Dosage 0.075%: GLY (A), LG650 (B), Glucose (D), Dosage 0.1%: PG (C).**

**Table 3: Total heat evolved after 22 hours.**

Product	Dosage (%)	Total heat (J/g)
No grinding aid	--	262
TEA	0.015	265
	0.075	273
	0.1	260
	0.15	263
Glucose	0.075	240
GLY	0.075	262
LG650	0.075	258
PG	0.1	276

#### **4. Conclusion**

The data presented here on the influence of polyols on the properties of cement offer interesting perspectives for the use of these additives as clinker grinding aids. Since the influence of these additives on powder dispersion (fluidification) and cement hydration both depend on the molecular structure of the polyols, the latter can be selected to provide a desirable cement behaviour in a particular grinding aid formulation. The changes induced by the polyols on the cement fluidity seem related to fairly simple chemical and structural characteristics of the molecules, which should be readily confirmed through model calculation of surface-molecule interactions. In the case of polyol effects on hydration kinetics, more systematic data will be required to establish mechanistic hypothesis.

#### **Acknowledgements**

The authors would like to thank Handy Chemicals Ltd, Ciment Québec and the Ministère de l'Industrie, du Commerce, de la Science et de la Technologie (Programme Synergie) for their financial support. In addition, the authors would like to thank Cailin Tang for his assistance in some of the measurements.

## References

- [1] Morasse, S., Mécanisme d'action des agents de mouture pour les matériaux cimentaires, Ph.D. thesis, Sherbrooke, Canada, 168p (2000)
- [2] Moorer, H.H. and Anderegg, C.M., Cement grinding aid and pack set inhibitor, US Patent 3 615 785 (1971)
- [3] Moorer, H.H. and Anderegg, C.M., Cement grinding aid and set retarder, US Patent 4 204 877 (1980)
- [4] Arfaei, A., Berke, N.S. and Jeknavorian, A.A., Hydraulic cement set accelerating admixtures incorporating glycols, US Patent 5 340 385 (1994)
- [5] Cheung, J.H. and Gartner, E.M., Grinding aid composition and cement product, US Patent 5 429 675 (1995)
- [6] Teoreanu, I. and Guslicov, G., Mechanisms and effects of additives from the dihydroxy-compound class on Portland cement grinding, Cem. Conc. Res., **29**, pp 9-15 (1999)