New foamed/modified bitumen using phosphogypsum waste

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ABSTRACT

This paper describes a new alternative way to produce foamed bitumen, by using phosphogypsum wastes (PG), which is also able to enhance the mechanical behavior of the resulting binder. PG waste is generated worldwide from the production of phosphoric acid and deposited in stacks, causing environmental problems.

The results obtained point out that the addition of 10 wt.% PG to a 35/50 paving grade bitumen, when activated with a small amount of strong acid, results in a foamed bitumen with enhanced the rheological properties, especially at high in-service temperatures, after foam collapses. This is mainly attributed to the existence of chemical reactions involving phosphorus compounds contained in the PG, forming new chemical links with some bitumen molecules.

Another positive aspect of this technology is that this method produces more stable bitumen foam if compared to the traditional processes, i.e. through direct injection of water. Thus, the combined effect of temperature and the activation agent (sulphuric acid) gives rise to dehydration of the structural water contained in PG yielding foamed bitumen.

Keywords: Additives, Foam, Modified Binders, Rheology, Waste

1. INTRODUCTION

Phosphate production generates huge amounts of wastes since each ton of phosphoric acid is accompanied by the production of 5 tons of phosphogypsum.

Phosphogypsum is a form of gypsum (calcium sulphate) formed as a by-product in the manufacture of phosphate fertilizers in which phosphate ore is reacted with sulphuric acid and water to produce phosphoric acid[1]:

$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4{\cdot}2H_2O + HF$ (R1)

PG consists primarily of calcium sulphate and contains some impurities such as P_2O_5, F^-, organic substances, heavy metals and minor amount of the so-called naturally occurring radioactive materials (NORM).

A literature review shows that some studies have been carried out on the reuse of phosphogypsum wastes in several applications. It worth mentioning it potential use as an agricultural fertilizer, in soil stabilization amendments [2], in the cement industry as a setting regulator in place of natural gypsum [3], or as a raw mineralizer in the burning Portland cement clinker [4].

Unfortunately, the presence of the mentioned impurities can negatively affect the performance of phosphogypsum in some of the above applications and puts restrictions on the reuse of PG so that cannot be used as a replacement of natural gypsum in the housing industry.

Regarding road pavements, some possible applications of PG have been proposed such as road base and subbase material [5]. However, this alternative presents a high risk of leaching contaminants present in phosphogypsum into the surrounding environment.

Here, PG is directly used as a bitumen modifier aiming to take advantage of the remaining fraction of phosphorous compounds that were not extracted during the fabrication of phosphoric acid. In this sense, it has been widely reported in the literature that phosphorous compounds, especially polyphosphoric acid, give rise to a remarkable modification in the mechanical behaviour and microstructure of the resulting bitumen [6].

Additionally, the crystallization water included in PG may also be used to produce a foamed bitumen in order to improve the coating of binder on aggregate. In this sense, this foaming process is similar to others that use a hydrophilic "filler", zeolites (which contain about 20-25% of water of crystallization), etc. Regarding the environmental concerns, it is worth mentioning that bitumen constitutes a consolidated way for immobilizing wastes because of its waterproofing characteristics [7].

2. EXPERIMENTAL

Bitumen supplied by Construcciones Morales (Spain), with a penetration of 40dmm and ring and ball softening temperature of 52 ºC was used as base bitumen. Binder was mixed, at 150ºC, in a low shear device, with different additives at concentrations and processing conditions shown in Table 1. Phosphogypsum (PG) sample was supplied by the Fertiberia Huelva factory (Spain), and H_2SO_4 and commercial gypsum, $CaSO_4{\cdot}2H_2O$ (CG), were supplied by Panreac, S.A. (Spain). For the sake of comparison, a reference bituminous sample containing 3 wt.% commercial SBS Kraton D1101 (“SBS-reference” sample) was also prepared.

Table 1. Nomenclature, additive concentration and processing conditions of the samples studied.

Name	Additive	[wt.%]	Proces. time (min)
SBS	SBS	3	120
PG	PG	10	60
CG	CG	10	60
PG- H_2SO_4	PG H_2SO_4	10 0.5	60
CG- H_2SO_4	CG H_2SO_4	10 0.5	60

H_2SO_4	H_2SO_4	0.5	60

Penetration and ring and ball softening temperature were determined according to EN 1426 and EN 1427, respectively.

Viscous flow measurements, at 60 ºC were conducted on the bituminous samples using a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria). Serrated plate-and-plate geometry (25 mm diameter and 1 mm gap) was always used.

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian, USA) apparatus. Neat bitumen and modified binders solutions were prepared by dissolving 0.7 g of each sample in 25 mL dichloromethane. The same volume of solution was always laid on a potassium bromide disk (32×3 mm), which was then exposed to ambient until the solvent was completely evaporated. Afterwards, the KBr disk was placed into the appropriate sample holder and the FTIR spectra were obtained in a wavenumber range of 400–4000 cm^{-1}, at 4 cm^{-1} resolution, in the transmission mode.

Finally, foaming tests at 150ºC, were conducted on a model sample containing 10 wt.% PG and 0.5 wt.% H_2SO_4. For the sake of comparison, a traditional foam was tested, by adding 2 wt.% water to a neat bitumen at the same temperature. Samples were stirred, at 500 rpm, for 30 s. Agitation was then stopped, and the foaming process was followed. Readings taken by the laser device DLS-C 15 distance laser sensor (Dimetix AG, Zurich, Switzerland) determined the evolution of the foam height with time.

3. RESULTS AND DISCUSSION

Figure 1 shows the viscous flow curves, at 60 ºC (maximum expectable temperature reached in a pavement), for modified binders. All the systems present a Newtonian region, at low shear rates, followed by a shear-thinning drop beyond a threshold value of shear rate.

As may be observed in Figure 1, the addition of both phosphogypsum and commercial gypsum hardly modifies the viscous response. This fact hints that PG and CG act merely as a “filler” and do not interact with the bituminous matrix. Conversely, only if a small amount of sulphuric acid is added (0.5 wt.%) a notable increase in viscosity of more than one order of magnitude is pointed out (“PG-H_2SO_4” sample). From a rheological point of view, since this modification gives rise to increased Newtonian viscosities and lower values of the limit shear rate which marks the onset of the shear-thinning region, activated PG (with a strong acid) produces the development of a more complex microstructure as previously reported [7].

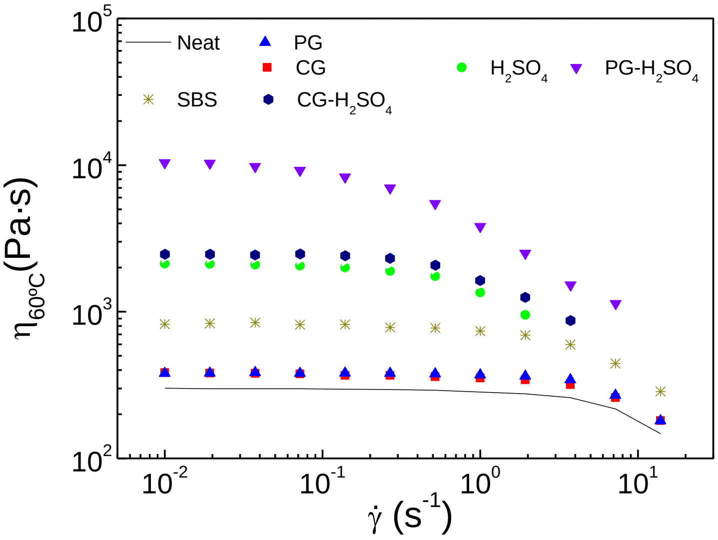

Figure 1: Viscous flow curves, at 60 ºC, for the neat bitumen and the different

modified binders studied

In order to analyse the origin behind the high level of modification observed after addition of sulphuric acid to the phosphogypsum modified bitumen, two more samples were prepared. Firstly, commercial gypsum modified bitumen (major component of phosphogypsum) was mixed with the same amount of sulphuric acid, at 150 ºC ("CG-H_2SO_4" sample), and secondly, a bitumen was solely modified with sulphuric acid ("H_2SO_4" sample) and, their flow behaviour were evaluated as well.
Thus, as can be observed in Figure 1, flow curves for these binders were quite similar and clearly below "PG-H2SO4" sample. Consequently, it can be deduced that even though sulphuric acid produces a notable change in the flow response, in the case of phosphogypsum the modification is mainly attributed to some of the compounds contained in the PG fraction (supposedly phosphorous compounds and not $CaSO_4$ which is about 8 wt.%) activated or extracted with the presence of the acid. This provokes the observed viscosity enhancement, at 60 ºC, of more than one order of magnitude if compared to the "SBS-reference" sample. This result represents by far a larger degree of modification than that corresponding to the "SBS-reference" sample.

Name	**Pen. (dmm)**	**$T_{R\&B}$ (ºC)**
Neat	40	52
SBS	33	56
PG	35	54
CG	36	54
PG- H_2SO_4	21	69
CG- H_2SO_4	30	59
H_2SO_4	31	58

Table 2. Penetration and ring and ball softening point, for the neat bitumen and the different modified binders studied.

The technological characterization performed, which included penetration and R&B softening temperature tests, is presented in Table 2. Once again, the addition of CG or PG without sulphuric acid leads to a not very significant modification of both properties. As expected, the addition of 0.5 wt.% sulphuric acid produces a remarkable decrease in the penetration value, as well as an increase of 6 ºC in the softening temperature. However, when this acid is added on a sample which has been previously modified with phosphogypsum synergic effects are clearly pointed out. Thus, penetration is reduced to a half of the corresponding to the neat bitumen's value, whereas softening temperature increases 17 ºC and, consequently, the activation of PG with sulphuric acid provokes by far the largest degree of modification.

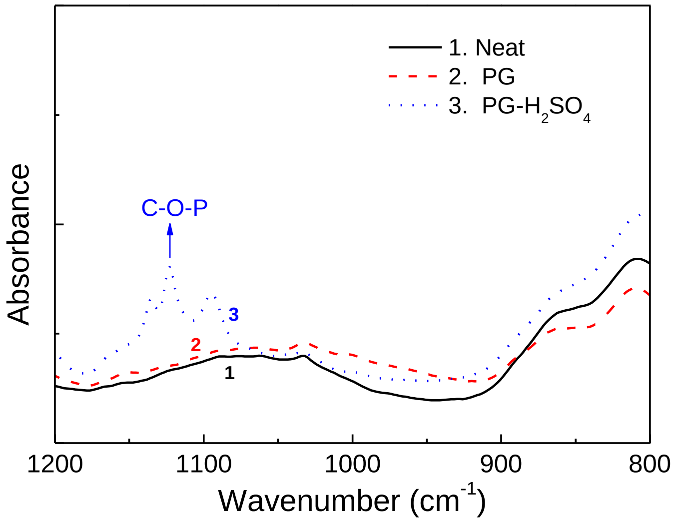

Figure 2: FTIR spectra for the neat bitumen and selected modified binders

Finally, FTIR spectroscopy carried out on selected samples (Figure 2) demonstrates the existence of chemical reactions between phosphorus contained in the PG fraction and some bitumen compounds (only with the presence of small amount of sulphuric acid). Thus, only the "PG- H_2SO_4" sample displays a new absorption band, from 1060 to 1180 cm^{-1}, which has been related to C−O−P vibrations as a consequence of new bonds formed by chemical modification. Therefore, this fact would explain the enhancement in the rheological response [6-7].

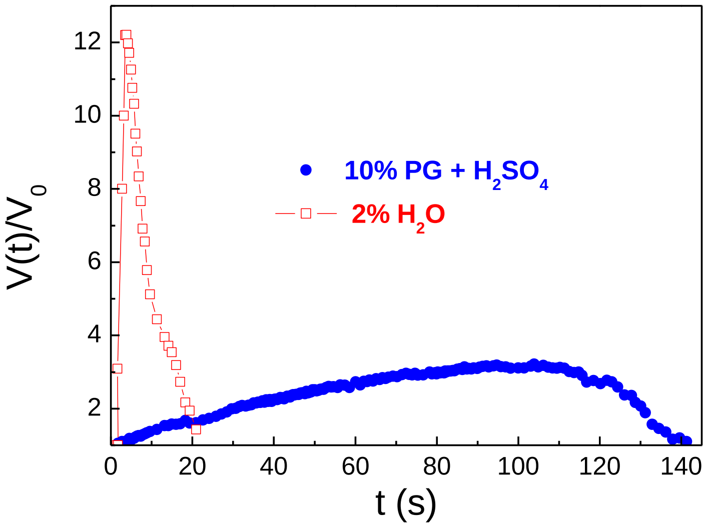

Figure 3: Expansion ratio for sample PG-H_2SO_4 compared to the direct addition of water to the neat bitumen

Finally, Figure 3 points out the foaming capacity of PG during processing compared to a traditional process in which cold water is directly added to the expansion chamber, at 150ºC. Thus, the release of the crystallization water contained in PG (approximately 20wt%) is confirmed by the bitumen foams obtained. As may be seen, the binder volumetric expansion ratio, V(t)/Vo (where V(t) is the foam volume measured at each time and Vo is the initial binder volume), undergoes a maximum due to the vaporization of hydration water. It should be noticed that even though the maximum expansion ratio is lower than the one obtained by direct addition of water, the foam stability is remarkably improved. This outcome is clearly deduced from foam half-life values (the time required for the foam column decaying to 50% of its initial height) since it is more than10 times higher in the case of PG (131 s for PG- H_2SO_4 and 9 s for direct water addition). In addition, the “Foam Index” (FI) is also considered [8-9]. The Foam Index is a measure of the area under the decay curve i.e. the change in expansion ratio with time, which reflects the stored energy in the foam for specific bitumen foamed at a known temperature. Here, for PG- H_2SO_4 FI is more than three times higher if compared to the traditional process (335 and 105 respectively) and, as result, this new foaming method presents improved stability.

As a summary, phosphogypsum may be used as a bitumen modifier for paving industry. Moreover, the crystallization water of PG is released during processing in such a way that foamed bitumen is obtained. This new foaming process yields foams with improved stability and, therefore, can be potentially used in road recycling technologies. Unlike traditional foamed bitumens obtained by direct injection of water, by using PG, the binder that results after the foam collapse presents significantly improved performance.

All these results may encourage industry to envisage the use of phosphogypsum wastes in paving applications. Thus, apart from the benefits for the bitumen performance, it may constitute an alternative way of managing this kind of residue and an efficient manner of immobilizing these low/intermediate radioactive wastes. However, this is only a preliminary study since the interaction with mineral aggregates, water resistance, etc., need to be evaluated before industrial use.

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