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A comparison between the influence of superplasticizer and organosilanes on different properties of cemented paste backfill

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HIGHLIGHTS

- Vinyl and methyl silanes provided the water repellency influence on CPB.
- Vinyl silane provided the highest water repellency effect over the rest of admixtures.
- Vinyl and methyl silanes plus polycarboxylate superplasticizer boosted the UCS values.
- The type of tailings affected the effectiveness of organosilane to develop strength.

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ABSTRACT

The water repellency influence of non-polar organosilanes (vinyl and methyl) and polycarboxylate superplasticizer were studied and compared on flow behavior, strength development, and microstructural properties of cemented paste backfill (CPB) composed of sulfidic and non-sulfidic tailings. The addition of water-repellent admixtures affects the water requirement and hence the total performance of cementitious materials. Based on the uniaxial compressive strength (UCS) test and slump height measurements, the addition of vinyl silane to CPB provided a higher UCS value and reduced the required amount of water for a specific slump height. The addition of vinyl and methyl organosilanes, however, was less advantageous on CPBs composed of sulfidic tailings since reduced the early strength development. The achieved differential thermogravimetric (DTG), mercury intrusion porosimetry (MIP), and scanning electron microscopy (SEM) results implicated that the use of vinyl silane was more efficient to densify the CPB matrix due to the hydration improvement and the formation of additional C-S-H gel specifically in non-sulfidic CPBs.

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1. Introduction

A wide range of organic, polymeric, and nano-sized admixtures (additives) such as water reducing agents are used to influence different properties of cementitious materials [1,2]. The addition of such additives in solids or liquids forms can influence the liquid/solid phases or liquid-solid interface of cement-based materials [3]. The organic and inorganic admixtures may bond and or reinforce the calcium silicate hydrate (C-S-H) structure or react with calcium hydroxide (CH) as the second major product of cement hydration to generate additional C-S-H gel (pozzolanic reaction) [2,4]. In addition, the nano-based admixtures (e.g., silanes) can fill

the nano-pores of C-S-H and reduce the total porosity and improve the compactness [5,6].

Organofunctional silanes are composed of a monomeric silicon-based molecule (nano-size) and four constituents including at least one organic attached group to the silicon molecule directly or through the organic bridges. The condensation and hydrolysis of silane coupling agents will polymerize large metal-containing molecules that may reinforce the cement-based materials [7–9]. A typical structure of an organofunctional silane is shown in Fig. 1.

Methyl and vinyl silanes consist of a non-hydrolysable/non-reactive/non-polar and covalently bonded organic group (R) to the silicon molecule. In the presence of water, the reactive groups of organosilanes (X) hydrolyze and form a high reactive silanol (SiOH) networks that later can be condensed and form siloxane covalent linkages similar to backbone polymer [11–15]. In cementitious materials, the bonding ability of siloxane linkages with the

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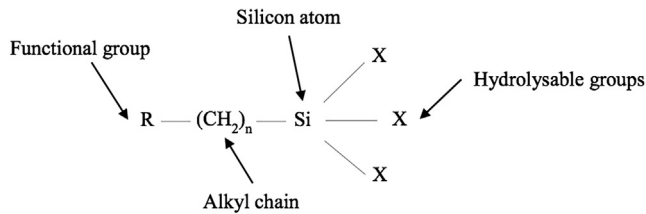


Fig. 1. Typical structure of organosilanes [10].

hydrated cement products (e.g., C-S-H) will decrease the structural phase separation tendency, [16] thus the mechanical strength development can be improved [17]. In addition, the non-reactive methyl and vinyl organic groups provide the water repellency influence while decreasing the required water for a specific slump height and improving the total flow behavior of cementitious materials [18,19].

Superplasticizers are water reducer and dispersive agents that are often used in cementitious materials for workability and compressive strength improvement. They adsorb on the surface of hydrating cement grains and release the trapped water by van der Waals forces and electrostatic charges during the initial hydration process [20–22]. Polycarboxylate ether-based superplasticizer (PCS) established a new generation of anionic comb-like polymer with backbone and side branches. Adsorption of PCS to the cement grains is mediated by carboxylate groups while dispersing effect of PCS originates from repulsion effect of long ether-group chains [23].

Cemented paste backfill (CPB) is an effective mine tailings management technique that can deliver a considerable amount of produced tailings from the mineral processing plant to the underground stopes and voids for secondary ground support and environmental concerns [24–26]. CPB consists of filtered mill tailings (75–85 wt% solids), mixing water (15–25%), and binding agents such as cement (typically 2–9 wt% of tailings' dry mass). No direct income will be gained from CPB since being a sort of waste management, thus mining companies attempt to reduce the pertinent costs more importantly by reducing the binder usage. In this case, CPB becomes a low strength material (UCS ~0.2 to 4 MPa up to 90 days), depending on the type and ratio of binding agent(s), grain size distribution, and mineralogical composition of mine tailings [27–29]. Since being delivered via pumping or gravity, CPB should have a proper flowability in order not to block or settle in pipelines (a typical slump equal to or greater than 180 mm is necessary for smooth flow when the standard slump cone was used) [30]. Therefore, the preparation of CPB requires a considerable amount of water that increases the water-to-cement (*w/c*) ratio to an exceeded level (generally *w/c* ≥ 3) that will affect the curing and the quality of the microstructure [31,32].

The novelty of the present study was to use two water repellent non-polar organosilanes (vinyl and methyl) plus polycarboxylate ether-based superplasticizer in CPB while the achieved results were compared to deepen our understanding regarding the use of such admixtures in cementitious materials and waste management. The aim was to legitimate the use of new water repellent agents in CPB that may be more beneficial over the regular water reducers.

2. Materials and methods

2.1. Materials

Two different types of tailings including a sulfidic (LaRonde, Quebec, Canada, specific gravity = 3.7) and a non-sulfidic (Goldex, Quebec, Canada, specific gravity = 2.6) were used in this study. Fig. 2 shows the similar particle size distribution of both tailings samples measured by Malvern Mastersizer laser particle size analyzer.

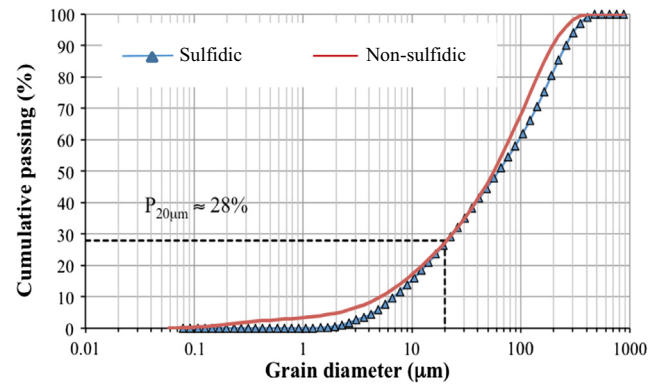


Fig. 2. The particle size distribution curves of both used tailings.

Table 1

ICP-AES analysis and XRD quantification results for the used tailings.

Element	ICP-AES analysis (%)		XRD quantification (%)		
	Sulfidic	Non-sulfidic	Mineral	Sulfidic	Non-sulfidic
Al	4.5	7.7	Quartz	46	18
Mg	0.36	1.4	Muscovite	9	8
Ca	0.75	3.4	Gypsum	3	–
Fe	17.9	2.2	Pyrite	26	0.7
Ti	0.03	0.04	Chlorite	8	8
Zn	0.22	–	Paragonite	6	–
S	13.8	0.2	Calcite	–	8
K	0.6	0.5	Albite	–	55
Na	0.1	3.6			

Table 2

The main characteristics of used silanes.

Chemical Agent	Appearance	Specific gravity (25 °C)	Color
Methyl-silane	Clear liquid	0.95	Transparent
Vinyl-silane	Clear liquid	0.97	Transparent
Superplasticizer	Viscous liquid	1.1	Brown

Table 1 presents the results of both XRD and ICP-AES analyses of used tailings. Both tailings were largely composed of silicate-based minerals, including quartz, chlorite, and albite correlating properly with the elemental compositions obtained by ICP-AES.

Three types of water reducing admixtures including Polycarboxylate ether-based superplasticizer (PCS-PS-1466, from BASF Chemicals), vinyl-trimethoxy silane (VTMS-XIAMETER®OFS-6300, from DOW Chemicals), and methyl-trimethoxy silane (MTMS-XIAMETER®OFS-6070, from DOW Chemicals) were used in this study (Table 2).

Ordinary Portland cement for general use (GU) was used as the only binding agent type in this study. Table 3 presents the results of XRD analysis and the physical properties of the Portland cement used in this study (C₃S: Tricalcium Silicate, C₂S: Dicalcium Silicate, C₃A: Tricalcium Aluminate, C₄AF: Tetracalcium Aluminoferrite). In addition, potable municipal water (tap water) was used to prepare all the CPB mixtures.

The CPB specimens were prepared with 3 and 4.5 wt% binder content (based on dry mass of tailings) and the amount of admixture was calculated based on the binder mass. The preparation procedure starts with the blending of dried tailings and binder while the tap water was slowly added until the mixture reached a solid concentration of 76% (Table 4). Basically, a 70–85 wt% solid concentration is suitable for the preparation of CPB to be deliverable via gravity or pumping through the pipelines [31]. All the triplicate CPB specimens were prepared for the three curing times including 3, 7, and 28 days and poured into cylindrical polyvinyl molds (having 50.8 mm diameter and 101.6 mm height), then sealed and left to cure.

2.2. Experimental methods

The influence of admixtures on the CPB's flow behavior was estimated by slump height measurement using a small Abrams cone (having the half of the height of standard slump cone using ASTM WK27311) [33]. The initial slump height of all the specimens was fixed at 74 mm before the addition of water reducers; next, the specific admixture was added to the mixture and blended while the new slump

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