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Cementitious backfill with high sulfur content Physical, chemical, and mineralogical characterization

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Abstract

Use of cemented backfill in underground mining is common practice. The major economical benefits include increased recovery of ore and a reduction in the volume of waste requiring surface disposal. This paper presents new studies into the behavior of cemented backfill, namely, the chemical and mineralogical changes (weathering) with time that affect the mechanical strength of the fill. The weathering mechanism typically consists of sulfate attack. This process can occur rapidly during curing and depends on the binding agents used. The reaction involves dissolution of hydrated calcium phases followed by formation of expansive phases resulting in the degradation of the backfill's mechanical properties. The use of fly ash, which is resistant to sulfate attack, generally reduces any strength deterioration. These phenomena are illustrated with a case study that demonstrates the influence of these alterations on the long-term mechanical properties of a cemented paste backfill sampled in situ.

Keywords: Characterization; Scanning electron microscopy; Mechanical properties; Durability; Sulfate attack

The development and utilization of paste backfill technology has been evolving over the last two decades around the world and especially in Canada. The mining industry was particularly interested in the technology for reducing costs associated with backfilling large open stopes. Paste backfill can serve as a construction material to create a floor to mine on top of, a wall to mine next to, and a roof or headcover to mine under [1]. Another attractive aspect is that a large amount of tailings can be disposed underground (up to 60%). This is a significant environmental advantage, especially when tailings are acid generating. Paste backfill consists of dewatered tailings with up to 7 wt% binder added. Hydraulic cements normally are used as binder agents, such as ordinary Portland cement (OPC), fly ash, blast-furnace slag, or a combination of these.

It is well known [2–6] that the presence of sulfur species within cementitious material can cause a deterioration in quality for construction works (e.g., mortars and concrete in the building trade). The same phenomenon has been observed in many sulfur-rich backfills. The high sulfide and low cement contents enhance the reaction. Calcium-rich cements like OPC have many disadvantages due to their weak resistance to sulfide attack on the cement bonds [7]. Hydration of anhydrous calcium species leads to formation of portlandite [$Ca(OH)_2$], which is a very unstable mineral even for small pH variations. C-S-H gels (or tobermorite when crystallized) and various calcic sulfoaluminate species are the other more common hydrated phases of the cement, and they are more stable than portlandite. Fly-ash–based cements generally are used to avoid the deleterious effects of sulfur species, by favoring pozzolanic hydration reactions that consume portlandite to form more C-S-H gels. In addition to the presence of sulfur in the backfill, the relatively low binder content in the backfill causes significant dilution of the cement, which may lead to the following two negative consequences:

1. pH buffering (which generally is around 12.5 as fixed by the portlandite) becomes vulnerable,
2. Entanglement of hydrated phases is greatly affected by the abundance of grain residue in the mixture. This factor will directly affect the cohesion of the backfill.

The hydrated phases can be endangered rapidly as a result of sulfidic mineral reactivity. This reactivity is facilitated by the degree of saturation of the paste and the presence of oxygen. The consequence is a progressive decrease

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in pH accompanied by dissolution of hydrates (and release of hydroxyl ions (OH^-) according to their solubility and buffering effect order). Sulfide oxidation in alkaline media is accompanied by consumption of hydroxyl ions and formation of metal (e.g., iron) hydroxides. At an advanced level, the cement loses all buffering potential. The cement matrix then consists of gypsum and hydroxides (iron, silica, aluminum) only. Anhydrous C_3A presence within the backfill is less probable because of the high water-to-cement ratio (up to 3.5) generally imposed by the maximum solids content.

The main objective of this work is to relate mechanical strength and chemical stability through a case study. The underground mine chosen is localized in the Abitibian region of Quebec, Canada. The polymetallic ore is mined and processed for copper, zinc, gold, and silver recovery. After concentrate extraction, large tailings tonnage is generated with a high acid mine drainage potential. About 50% of the tailings are pumped to the tailings dam and the remaining material is used as high-density cemented paste backfill [8]. An experimental procedure has been implemented to study the mechanical stability of paste backfill sampled at the mine (freshly produced at the backfill plant or cored into the filled stope) and to establish the relationship between the interpretations achieved using the “q-p” mechanical criterion (the parameters p and q are the mean stress and the deviatoric stress, respectively, acting on a sample during the compression test) and those obtained from the microscopic examinations and geochemical analysis. Another objective consists mainly in defining the nature of the hydration that occurs under the backfilling conditions at this mine.

1. Experimental program

1.1. Materials

Pyrite is the principal sulfide mineral in the Abitibian tailings studied. Sulfur content is highly variable (approximately 10 wt% on average). The binder is a mix of fly ash (40%) and OPC (60%). Tailings are dewatered using a conventional thickener-filter method and mixed with the binder (4.5% of the total dry weight) in a spiral mixer. The solids content of the final mix, which is pumped underground for use as backfill, is approximately 80 wt%.

Samples for mechanical tests and other analyses were collected from the backfill plant (molded in cylinders and cured in the laboratory) and from in situ cores sampled from a stope. A diamond rotary drill equipped with a triple tube system was used to recover in situ samples, which were 100 days old. Clay mudstone was used as drilling mud to avoid dissolution of cement and perturbation of the samples. In fact, experience has shown that this kind of material can be easily remoulded in the presence of water, thereby complicating the drilling procedure [9,10]. The core was about 6 cm in diameter. To prevent evaporation and protect the sample from oxidation, cores were covered with paraffin film and stored in a controlled atmosphere chamber until their utilization for tests or analysis.

To better understand the geochemical behavior during backfill weathering, equilibrated solution samples were extracted for chemical analysis. The first type of solution was the make-up water from the mill; the second type was a residual solution extracted from samples at different curing times (1 and 8 days); and the third solution was collected from drains in the filled stope.

1.2. Methods

The investigation included two main aspects: a physical/mechanical characterization and a chemical/mineralogical characterization. This elaborate laboratory test program was implemented to study the relation between the loss of paste backfill strength and its degree of chemical weathering.

As a first step, the following tests were used to characterize the material:

- Specific gravity determination,
- Particle size measurement,
- Void ratio calculation, and
- Triaxial compression tests: normally consolidated (drained).

This laboratory program focused on the main physical characteristics of the backfill and how these characteristics changed with time and cement content. The triaxial tests were done using a Tinius-Olsen (USA) (50,000 kN max load) press and the tests were sheared with a nominal strain rate of 1 mm/min.

As discussed, chemical and mineralogical analyses were completed on the solid and the interstitial solution of backfill samples (chemical analysis only). Chemical analyses were performed by induced coupled plasma spectroscopy at the Environmental Laboratory of Noranda Inc., Quebec, Canada. Small-scale microscopic examinations of the solid samples were conducted using a scanning electron microscope (SEM; Hitachi S-3200-N, Japan) by energy dispersive spectroscopy (EDS) from Link-Oxford-ISIS-300 (England). X-ray microanalysis allowed semiquantification without use of external standards and a detection limit of less than 1% with a confidence interval of ±0.5%. Oxygen was estimated by oxide stoichiometry [11]. Analyses were performed on freshly cut surfaces.

2. Results and discussion

2.1. Chemical and mineralogical characterization

The geochemical characterization of paste is a critical component of any material assessment, whether used for underground backfill or surface disposal. Chemical analyses were performed on the mine tailings before binder addition and on the binder reagent itself (Table 1). The calcium cement content is low compared to pure OPC. The mineralogical composition of the tailings was determined by cal-

Table 1
Chemical analysis of the tailings and binder agent

	Al (%wt)	C ti (%wt)	Ca (%wt)	Cu (%wt)	Fe (%wt)	Mg (%wt)	S (%wt)	SO_4 (%wt)	Si (%wt)	Zn (%wt)	K (ppm)	Mn (ppm)	Na (ppm)
Tailings	2.81	6	1.24	0.14	21.10	3.54	16.80	0.56	15.82	0.11	260	890	120
Binder	7.28	NA	27.3	NA	4.06	NA	1.36	NA	12.2	NA	NA	NA	NS

culation using the chemical analyses and theoretical stoechiometry of the minerals. The proportion of pyrite obtained in this manner was 31 wt%. The other sulfidic minerals identified were chalcopyrite and sphalerite, which were accessory and represented 0.42 and 0.17 wt%, respectively. The gangue minerals were mainly silicates and carbonate minerals estimated at 10 wt% by analysis of total inorganic carbon (C ti).

The chemical composition and the saturation index of dissolved species within the backfill pore water are the main factors that influence the cement-hardened paste crystallochemistry [5]. The equilibrated solutions described were analyzed for aluminum, silicon, calcium, iron, pH, alkalinity, and conductivity. The results are summarized in the Table 2.

Calcium (as hydrated lime) is added during the ore flotation process to maintain alkaline conditions. As the analytical results in Table 2 demonstrate, the solutions contain a large amount of dissolved sulfate produced during early sulfide oxidation (before ore processing). The main conclusions from the backfill equilibrated water analyses are:

- Cement components seem to buffer the backfill solution progressively, resulting in an increase in pH during short-term curing,
- Oxidation of sulfides occurs after placement, as demonstrated by a higher sulfate concentration in the water percolating from the stope,
- Absence of dissolved iron indicates that it precipitates in the backfill. Iron hydroxides are not soluble at alkaline pH [12].

The quantity of sulfate released has decreased after the first stages of cement hydration, probably because of the precipitation of gypsum, which can contribute to the binding processes. However, the solution coming from stope drainage is supersaturated regarding sulfates and is consequently very aggressive (DIN norm 4030).

2.2. Physical characteristics and mechanical strength

A quality control program was put in place to assess backfill plant performance. Backfill samples, once collected, were tested in the laboratory at various curing times (7, 14, and 28 days) to determine shear strength. Triaxial compression tests and unconfined compression tests were performed. The backfill samples were cylinders 20 cm high and 10 cm wide. The cylinders were placed in a controlled atmosphere chamber for curing. The void ratio and water content were measured for each cylinder after the compression tests. More detailed results were published previously [13,14]. The mean physical characteristics of the samples are presented in Table 3.

2.2.1. Control tests during operations

The mechanical characterization program at this mine included samples with cement contents ranging from 3% to 7% by weight. Fig. 1 illustrates some of the results from triaxial tests conducted on control samples. The strength increased with cement content, as expected. The cohesion on the q-p diagram is close to 300 kPa at 7% cement and reduces rapidly to less than 100 kPa at 3% cement. The unconfined compression strength varied from 500 kPa at 3% cement to 1200 kPa at 7% cement. In this diagram, the parameters are defined as:

$$q = (\sigma_1 - \sigma_2)/2 \qquad (1)$$
$$p = (\sigma_1 + \sigma_2)/2$$

where σ_1 is the major stress and σ_2 is the minor stress.

Based on the results of the strength testing, it was decided that the backfill would be made with approximately 5 wt% cement. This represents the most economical value with suitable cohesion to promote a free-standing backfill face when mining the adjacent secondary stope.

Table 2
Chemical characteristics of the backfill pore water

	pH	Conductivity (μΩ)	Alkalinity (kg CaCO3/t)	Al (mg/L)	Si (mg/L)	SO_4^{2-} (mg/L)	Ca (mg/L)	Total Fe (mg/L)
Mix water	9.42	2660	NA	NA	NA	626	515	ND
Water cylinder 1 day	9.63	26800	60	ND	3.6	687	328	ND
Water cylinder 8 days	11.23	26700	121	0.9	7.4	400	427	0.2
Stope water > 56 days	12.04	37900	302	0.3	3.5	1145	466	0.1

NA: not analyzed; ND: not detected.

Table 3
Mean physical characteristics of 50 samples

Residue grain size D 90	76 μm
Void ratio	1.0 e
Degree of saturation	90%
Percent solid by weight	78%
Paste slump consistency	19 cm

Table 4
Mean physical characteristics of 12 samples

	Mean	Ecart-type
Residue grain size D90 (μm)	76	—
Void ratio (e)	0.98	0.09
Degree of saturation (%)	91.91	2.45

2.2.2. Strength tests of core in situ samples

The cores from the in situ sampling program were tested to determine their saturation level and void index. Unconfined compression tests and triaxial compression tests were conducted on cylinders cut from these backfill cores. The results are presented in Table 4.

The backfill placed in the sampled stopes had been prepared with a cement content of 4.5% by weight. Test results on the in situ samples showed a very low cohesion as illustrated on the q-p diagram of Fig. 2. This was unexpected, because control samples for these stopes during the preliminary testing had shown a cohesion of 200 kPa after 28 days of curing. The strength of the backfill after 6 months was now much lower than the 28-day strength. To elucidate this phenomenon, an extensive chemical and mineralogical investigation program was initiated.

2.3. Backfill weathering

Backfill materials can be characterized as having a high porosity, but their hydraulic conductivity is generally low as influenced by cement and particle size (ranging from 2.5 to 28 cm/h [7]). Nevertheless, such values permit aggressive chemical solutions to flow throughout the sample and cause damage. The weathering processes include fluid transfers, solid/fluid interface reactions, capillary pressure, and crystalline growth [5]. Improvements to weathering resistance can be realized by limiting fluid transfer. Sulfide grains will then be protected from oxygen diffusion and chemical mobility. Sulfide oxidation (pyrite mainly) in cement media may consume hydroxyl ions ($OH-$) as described by the following reaction:

$$4\ FeS_2 + 15\ O_2 + 16(OH^-) \rightarrow 4\ Fe(OH)_3 + 8\ SO_4^{2-} + 2\ H_2O. \quad (2)$$

Binder (cement) reagent within the backfill material contributes to neutralization of the generated acidity until the alkaline hydrated phases are exhausted. The portlandite, C-S-H, and sulfoaluminate react in this order to ensure the neutralizing potential. The results of hydrate removal is the precipitation of iron hydroxides, and of secondary gypsum and/or ettringite $3CaSO_4 \cdot 3CaO \cdot Al_2O_3 \cdot 32H_2O$ when aluminate ions are available (from anhydrous C_3A or aluminosilicate dissolution). Both gypsum and ettringite are expansive phases. At pH under 9, all hydrated cement phases are dissolved. Cement-hardened paste then consists of gypsum and iron, silicon, and aluminum hydroxides only [6].

Macroscopic observations (Fig. 3) of the surface of a broken backfill core (sampled in situ) show a crack network distinguishable by its rust color compared to the rest of the

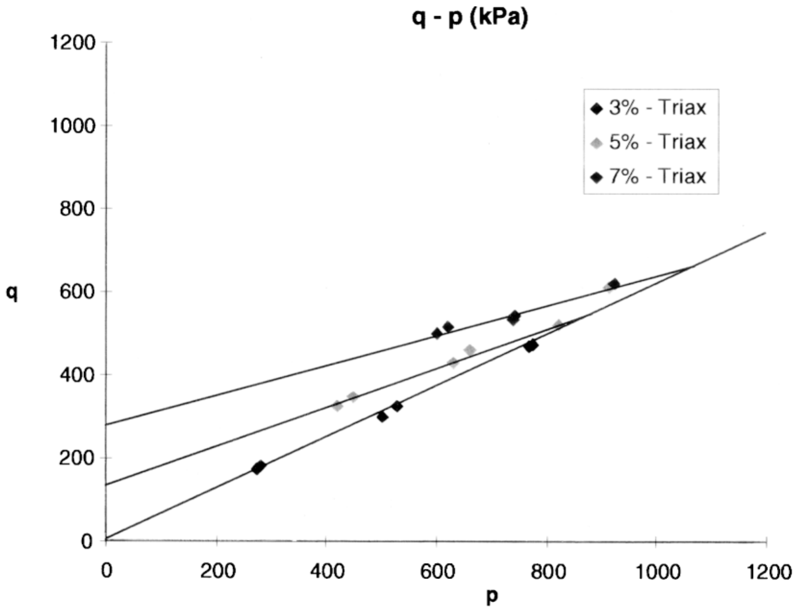

Fig. 1. q-p Diagram of triaxial compression tests on control samples.

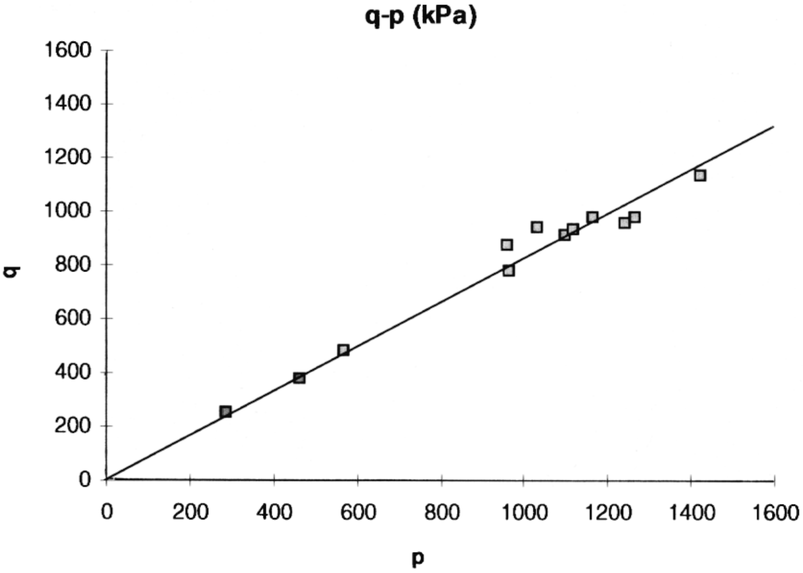

Fig. 2. q-p Diagram of triaxial and simple compression tests on in situ samples.

sample (gray color). This fissure network was the pore network for fluid circulation, probably inducing sulfide oxidation and iron hydroxide precipitation. The formation of this crack can be explained by crystallization of expansive phases.

Fig. 4 shows the global aspect of this backfill; the good tailings grain dispersion within the cement matrix (sulfides appear bright in the SEM backscattered image) and the apparent porosity reflecting the void ratio determined for this sample (Table 3). Detailed image (Fig. 5) shows that grain encapsulation is relatively good. However, the structure is still globally loose, resulting from the hydration conditions of this material. Moreover, well-crystallized phases (bar-shape mineral) can be seen easily at the microscopic level (Fig. 6).

To further understand the major weathering phenomena and to corroborate our assumptions, a series of EDS analyses were done to identify phase composition and to characterize the type of weathering by total surface analysis. The main observations were:

- Bars-shape minerals (Fig. 6) are exclusively gypsum,
- Hydrated cement phases were not found in this backfill sample,
- Comparative analysis (Fig. 7) of weathered surfaces (fissure planes) and fresh surfaces (bulk sample) highlighted notable chemical compositional variations.

Alongside the fractures, sulfur had been removed due to sulfide oxidation and sulfate production, as indicated by chemical analysis of the solutions extracted from the back-

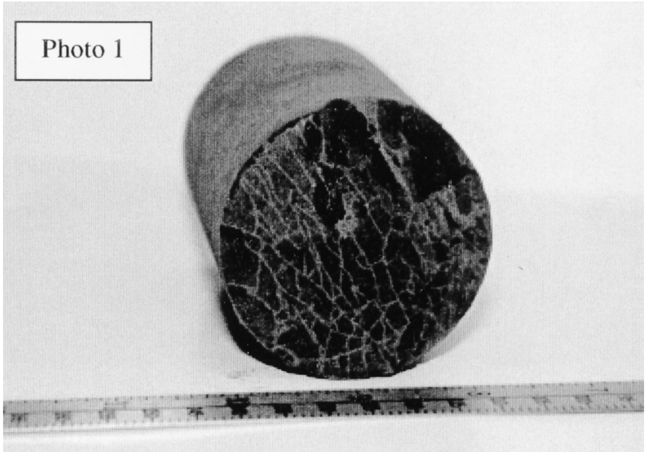

Fig. 3. Macroscopic view of an in situ backfill sample. Note the crack network. (Photo 1 of 4.)

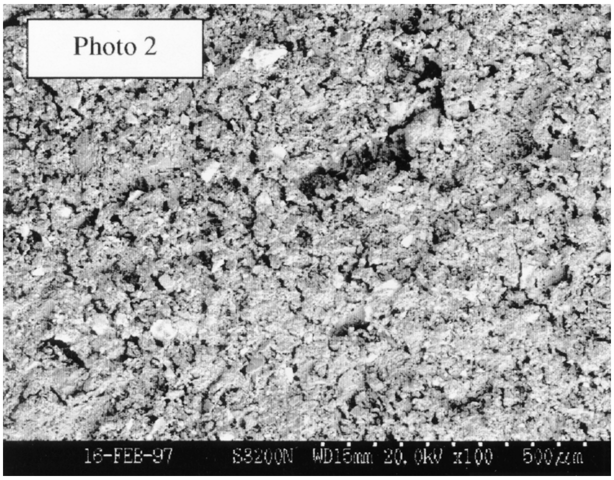

Fig. 4. SEM backscattered electron image. General aspect of backfill sample. (Photo 2 of 4.)

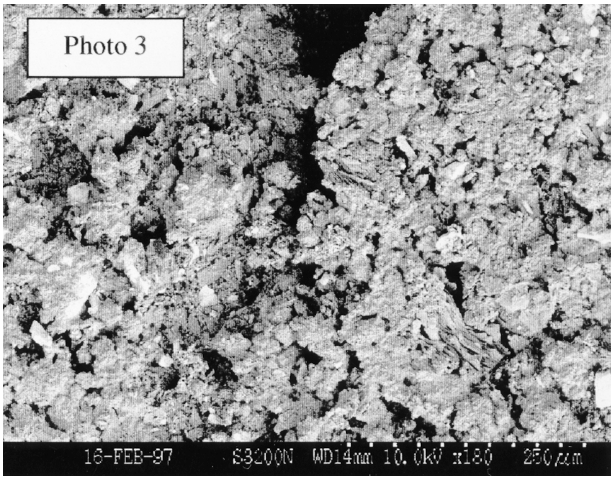

Fig. 5. SEM backscattered electron image. Detailed aspect of backfill sample. (Photo 3 of 4.)

fill studied. Iron was enriched because of its in situ precipitation as a hydroxide species, which caused the rust color, described previously. Calcium concentrations had been strongly decreased; only a small part of the calcium solubilized had precipitated as expansive gypsum. Silicon and aluminum precipitated as stable hydroxides after an important decalcification of the primary hydrated phases.

3. Conclusions

The investigations performed in this study showed that chemical alterations can seriously affect the long-term strength of backfill. These chemical alterations are not limited to a surface oxidation effect but can act throughout the whole backfill mass.

Analysis of core samples showed the presence of a fine system of fractures accompanied by oxidation traces, which are typical of a chemical weathering. Chemical and mineralogical analysis showed that the presence of sulfides in the tailings caused a dissolution of the calcic phases of the cement hydrates and promoted the formation of swelling phases, which in turn induced a deterioration of the cemented backfill.

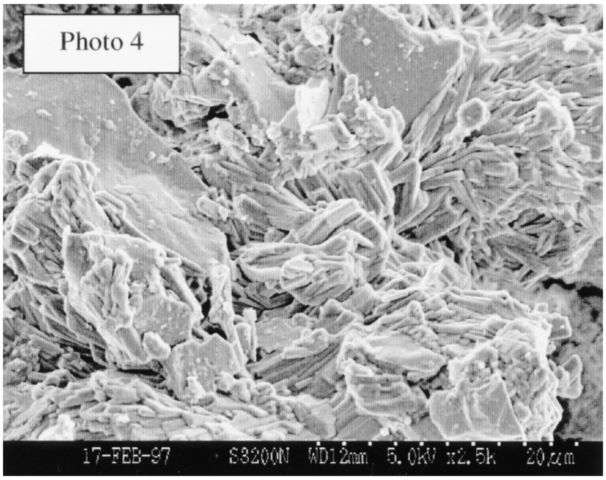

Fig. 6. Bars of gypsum encapsulating grain residue. (Photo 4 of 4.)

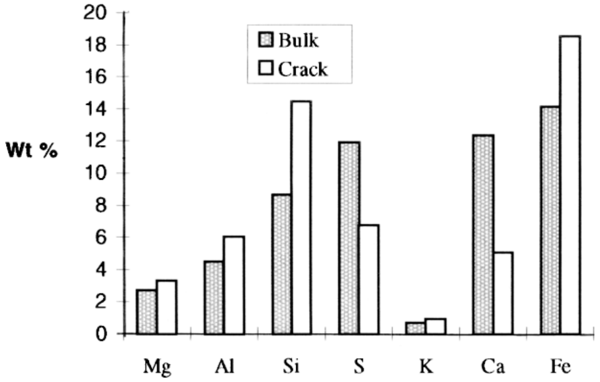

Fig. 7. EDS analyses of bulk and crack planes of the in situ backfill sample.

This short historical review of a paste backfill implementation experience illustrates the importance of a detailed study at the feasibility stage. Both mechanical and chemical aspects must be investigated. If any parameters are neglected, costly modifications can be required later on during operations. The long-term characteristics of the backfill must be considered. To have mechanical stability in the long term, chemical stability of the material must be ensured, as chemical alterations of the cement phases can have a negative impact on the strength of the backfill.

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