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REVIEW ARTICLE

Critical Review of Field Studies of Chemical Surface Coatings to Mitigate Leaching from Mining Wastes

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Abstract
Source control of mine drainage and leachate from mining wastes is ideal, but there is limited use of control methods aside from removal of wastes to repositories or capping wastes in situ. In some locations, neither removal nor capping is possible; thus, there is renewed interest in understanding technologies for coating mining wastes. This paper presents the current state of knowledge from a critical review of the few field case studies where chemical coating technologies have been applied to mined surfaces (e.g. a highwall) or mining wastes. It also includes laboratory studies where the same technology was examined on the same type of waste material as the field studies. The chemicals used in field studies for coating mining wastes were magnesium oxide, potassium permanganate, silicate compounds, phosphate compounds, and a furfuryl alcohol resin sealant. Descriptions of the methods employed, and results obtained are provided. Limitations of the individual studies and of the technologies in general are discussed. Potential reasons why coating technologies have not been commonly used are presented, along with further research needs.

Keywords Source control · Passivation · Microencapsulation · AMD remediation

Introduction

Mine drainage and leaching from mining wastes is commonly observed at abandoned mining sites around the world (Park et al. 2019; U.S. Government Accountability Office 2020). Water treatment at abandoned mining sites is generally costly and may be required in perpetuity to attain and sustain water quality standards (U.S. Government Accountability Office 2020). Source control is ideal, but there is limited use of control methods aside from removal of wastes to repositories or capping wastes in situ. Therefore, other source control techniques to minimize oxidation of sulfide minerals and subsequent leaching are gaining renewed interest in the United States.

Source control methods use physical or chemical barriers to isolate mining wastes or mined surfaces (e.g. a highwall) from oxygen and water or the addition of a bactericide to inhibit iron-oxidizing bacteria (Gusek et al. 2012; Kleinmann 1990; Kleinmann and Erickson 1983). Physical barriers include capping or covering mining wastes with materials and the configurations used depending on multiple factors, including site climate, hydrology, and reactivity of the waste (Mine Environment Neutral Drainage Program (MEND) 2004; Pabst et al. 2018). Chemical methods encapsulate or passivate pyrite or other sulfidic mineral surfaces to limit their oxidation (Kleinmann 1990) and may employ organic or inorganic chemicals (Park et al. 2019). Bactericides are effective at controlling iron-oxidizing bacteria and work best on fresh sulfidic minerals, but they are not used as a sole or permanent source control method because they can degrade or be leached from the mining waste (Skousen et al. 2000). While caps and covers have been used successfully to minimize leaching from metal mining wastes (e.g. Eger and Eger 2005; Nason et al. 2013), moving large amounts of capping material to remotely located (sometimes with only limited road access) waste piles at abandoned mine lands in mountainous regions is a logistical challenge and may be impossible without extensive earthwork to improve access (Nason et al. 2013; Priscu et al. 2010).

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An alternative to caps and covers is passivation or coating of mineral surfaces to eliminate or reduce their reactivity, but this method has not been used commonly at abandoned mining sites in the United States. This paper examines the current state of knowledge from a critical review of field case studies where coating technologies were applied to mined surfaces or mining wastes. Because few field studies were found, this paper also includes laboratory studies where the same technology was examined on the same type of waste material as the field studies. This critical review differs from other literature reviews of source control technologies, e.g. Park et al. 2019; Sahoo et al. 2013a; Tu et al. 2022, in that it focuses only on chemical coating technologies that have been applied in field settings, provides critical review of data and conclusions from the studies, and discusses potential reasons why chemical passivation technologies have not been used commonly at abandoned mining sites.

Methods

Sources used in this review are publicly available and include government reports, peer-reviewed journals, and conference proceedings. The literature search was conducted using Web of Science, Journal Storage (JSTOR), Science Direct, and Google Scholar to capture studies published through 2021. The following key words or phrases were used alone and in multiple combinations: adit, field study, microencapsulation, mine drainage, mined surface, mining waste, passivation, prevention, pyrite oxidation, remediation, source control, suppression, surface coating, tailings, tunnel, wall, waste dump, and waste rock. For studies having multiple sources, the most recent source was used unless an earlier publication had data not present in the most recent source, and preference was given to journal publications or government reports over conference proceedings. Technologies identified in field studies were alkaline chemicals, potassium permanganate, phosphate, silicate, and polymers. Silane and organic chemical technologies and microbially-induced coatings were found to have been studied in the laboratory, but no field studies were found; therefore, those studies are not included in this review.

Each study was critically reviewed for the method of application and technical quality following an approved quality assurance project plan. Performance data from studies having the following characteristics or issues were excluded:

- Technologies were used solely as amendments and coating formation was not targeted (i.e. only studies stating use as a coating were included).
- Technology was combined with a cap or cover, and only combined performance was reported.
- Methodologies or data were confusing or contradictory between text and tables or figures, or among multiple publications from the same authors.
- Studies having questionable comparability between leachate data from uncoated (controls) and coated materials (e.g. leached with different solutions).

The results section is organized by chemical or chemical group and presents descriptions of methods used in each study and the studies' performance data. Field studies are presented first in each section, followed by laboratory studies on the same type of mining waste. To evaluate coating efficiency, studies generally report differences in leachate pH and percent reduction (also called inhibition efficiency), which is the difference between concentrations or masses of AMD constituents (e.g. metals, sulfate) leached from treated materials and controls relative to the concentrations or masses leached from the controls. In instances where a reference did not present performance in this way, but data were provided for an appropriate control (i.e. differing only by not having the specific treatment), inhibition efficiencies were calculated from data in tables, graphs, or text; when an appropriate control could not be identified, only reported data were presented. Calculated inhibition efficiencies and data read from graphs using an engineer's scale are presented as approximate values, as is data reported as estimates in the literature cited. English units provided in cited sources were converted to metric units with the English units provided in parentheses. The discussion section includes a general comparison of technologies and presents limitations of the studies reported in the references and those observed in this review. The conclusion section summarizes key findings, provides possible reasons why coatings are not used commonly for source control, and presents further research needs.

Technologies

Alkaline Materials

Field

Although alkaline materials have been used alone or in combination as amendments (Mohamed et al. 2007; Trudnowski and Lewis 2004; Vandiviere and Evangelou 1998), as a cap (Nyström et al. 2019a, b; Sahoo et al. 2013b), or as a cap and cover system (Hallberg et al. 2005; Jia et al. 2015) for mining wastes, one field study was identified that assessed a coating that included caustic (NaOH) pretreatment followed by a solution of magnesium oxide (MgO) (McCloskey and Bless 2005). After raising the pH to > 11 by spraying ≈ 7,600 L (2,000 gal) of NaOH (normality not provided) onto a ≈ 15 m × ≈ 15 m (50 ft × 50 ft) section of a highwall at the Golden Sunlight Mine (MT, USA), the rock was sprayed with ≈ 7,600 L (2,000 gal) of magnesium oxide (MgO) solution (concentration not provided) formulated by the University of Nevada-Reno (UNR). Five equally sized and randomly selected treated and untreated areas were chosen for monitoring rinsate over time following the mine wall sampling technique developed for the Canadian Mine Environment Neutral Drainage Program (Morin and Hutt 2001); however, the number of sample locations decreased over time from highwall movement, unsafe conditions, or loss of sampling ports. One year after application, the pH of the rinsate was 3.4 from both the treated ($n = 1$) and untreated ($n = 2$) areas. The time-averaged (three sampling events) total sulfate (SO_4) concentration in the rinsate from the treated area was 21% less than from the untreated area, and the percent reductions in the cumulative total mass loadings per unit area were 38% (Al), 26% (Cu), -16% (Fe), 82% (Mn), 50% (Ni), and 75% (Zn) (McCloskey and Bless 2005).

Laboratory

McCloskey and Bless (2005) conducted triplicate laboratory humidity cell (HC) tests for 41 weeks (wks) on samples (size ≈ 0.64 cm × ≈ 1.3 cm (0.25 in × 0.50 in) of Golden Sunlight Mine highwall rock that were saturated in the field with MgO. At 41 wks, the average pH of the leachate was 6.57 from the treated rock and 2.81 from the untreated rock. Percent reductions in time-averaged concentrations were ≈ 100% (Fe) and ≈ 73% (SO_4). Average concentrations of Al, Cu, Fe, Mn, Ni, and Zn in leachate from the treated rock were below detection (< 50 µg/L) throughout the 41 wks. Average leachate concentrations from the untreated rock decreased over time for each element but remained approximately one (Cu, Ni, Zn), two (Al, Mn), or three (Fe) orders of magnitude higher than the detection limits at 41 wks (McCloskey and Bless 2005).

Potassium Permanganate

Field

Dupont Technologies patented a potassium permanganate-based technology (UNR-KP) that was tested on waste rock at the Gilt Edge Mine (SD, USA) by Trudnowski and Lewis (2004) and on highwall rock at the Golden Sunlight Mine by McCloskey and Bless (2005). The Trudnowski and Lewis (2004) study was conducted on ≈ 95.6 m^3 (125 yd^3) piles of waste rock placed into duplicate cells having dimensions of ≈ 12 m (40 ft) length × ≈ 3 m (10 ft) width × ≈ 1.5 m (5 ft) height at the front and ≈ 6 m (20 ft) height at the back. The bulk density of the waste rock was assumed to be ≈ 1.8 mt/m^3 (1.5 ton/yd^3) for an approximate mass of 170 mt. The technology was applied in two steps: the waste rock first was mixed with ≈ 0.0021 kg MgO/kg rock (4.1 lb/ton) and ≈ 0.00510 kg lime (CaO)/kg rock (10.2 lb/ton) and then loaded into the cells in ≈ 0.3 m (1 ft) thick lifts. After each lift was placed, it was sprayed with an aqueous solution of ≈ 0.00038 kg UNR-KP/kg rock (0.77 lb/ton) and ≈ 0.00014 kg NaOH/kg rock (0.29 lb/ton). Control cells were constructed in triplicate and contained waste rock having no chemical additions. Leachate from atmospheric precipitation infiltrating the waste rock was monitored March–October, 2001 and May–October, 2002; waste rock piles were frozen in the winter months (Trudnowski and Lewis 2004). For the highwall study, McCloskey and Bless (2005) raised the pH to 12 on a ≈ 15 m × ≈ 15 m section of the highwall with ≈ 15,100 L (4,000 gal) NaOH and then sprayed the wall with UNR-KP solution (dose not provided) and allowed it to cure (time not provided); sampling methods and the control data were the same as for their MgO study.

Leachate pH from the treated waste rock ranged from 3.81 to 10.05 but was generally between 6.5 and 8.8 during the study, compared to ≈ 2 to ≈ 6.5 from control cells (Trudnowski and Lewis 2004). The average percent reductions in dissolved leachate concentrations over the entire study time were reported as 99.97% ± 0.03% (Al), 99.99% ± 0.03% (Fe), and 73.43% ± 38.58% (SO_4). Except for one sampling date, dissolved arsenic (As) concentrations remained below the discharge limit of 190 µg/L, while leachate concentrations from the control units were ≈ 8 µg/L to ≈ 200 mg/L. Similarly, the concentration of dissolved Zn leached from the treated cells remained below the discharge limit of 338 µg/L but was ≈ 5 mg/L to ≈ 100 mg/L from control cells (Trudnowski and Lewis 2004). After 11 months (mos), the highwall rinsate pH was 3.4 from treated and untreated areas, the concentration of total SO_4 in rinsate from the treated areas was 34% lower than from untreated areas, and the percent reductions in cumulative total mass loadings per unit area were 62% (Al), 76% (Cu), 30% (Fe), 51% (Mn), 72% (Ni), and 76% (Zn) (McCloskey and Bless 2005).

Laboratory

Rock from the highwall was saturated in the field with UNR-KP and examined in triplicate HC laboratory tests by McCloskey and Bless (2005), similarly to their MgO study. At 41 wks, the average leachate pH was 6.5 from treated rock ($n = 5$) and 2.81 from untreated rock ($n = 2$). Percent reductions in time-averaged concentrations (mg/kg) were

≈99% (Fe) and ≈79% (SO_4). Average concentrations (mg/L) of Al, Cu, Fe, Ni, and Zn in leachate from the treated rocks were below detection after week 10 and Mn averaged 72 µg/L over the 41 wks, as compared to 4.09 mg/L in the control leachate (McCloskey and Bless 2005).

Silicate

Field

To facilitate formation of an iron silicate coating on pyrite surfaces, a buffered (pH 4–6) sodium silicate (Na_2SiO_3) solution is used with an oxidizer (Evangelou 1996). Vandiviere and Evangelou (1998) conducted a column (15 cm × 46 cm) study using sodium acetate (NaOAc) buffered Na_2SiO_3 and calcium hypochlorite ($Ca(OCl)_2$) as an oxidizer in a field setting. Fresh pyritic tailings from a metal ore processing plant (80% pyrite) and weathered coal spoil (21% pyrite) were first mixed with sharp sand (purity not provided) to give final pyrite contents of 4% and 19% by mass (authors did not indicate whether wet or dry), respectively. Several sets of duplicate columns were prepared for each material, with each having a portion of limestone ($CaCO_3$) to neutralize either 113.5% acidity (tailings only) or 9% acidity (both wastes). After placing 107 g $Ca(OCl)_2$ on top of each treatment column, the wastes were leached with a pH 5 (adjusted with HCl) solution of 0.1 M NaOAc and Na_2SiO_3 at concentrations of 30 mg/L Si (tailings only), 150 mg/L Si, or 300 mg/L Si. Control columns were prepared with the same masses of each mining waste and sharp sand, but without $CaCO_3$, $Ca(OCl)_2$, or NaOAc. Additional duplicated columns were set up for each of the limestone% neutralization groups having $CaCO_3$ only and $CaCO_3$ plus either 0.1 M NaOAc, 107 g $Ca(OCl)_2$, or 150 mg/L Si. After 1–3 wks, the columns were set up in the field and rainwater leachate was analyzed over time. After all the NaOAc had been leached out of the columns by rainfall (4–7 mos), *Thiobacillus ferrooxidans* were added to all of the columns to assess the effectiveness of the coating against microbial oxidation (Vandiviere and Evangelou 1998).

Percent reductions were not presented. For this review, percent reductions and propagated standard deviations in cumulative masses (mg) of Fe and SO_4 resulting from the silicate treatment (with buffer and oxidizer) were calculated using the data from the columns in each neutralization group (113% and 9%) having $CaCO_3$ only treatment (Vandiviere and Evangelou 1998). The columns having $CaCO_3$ only were used as surrogate controls to account for the influence of $CaCO_3$, which was not present in the experimental control columns and is not a component of the technology (Evangelou 1996). Data are presented in Table 1 for both the silicate study and the phosphate study discussed later.

KB-SEA™, developed by the Klean Earth Environmental Company (KEECO), is a silica microencapsulation technology for solid media that encapsulates metal-bearing solids in an impervious microscopic silica matrix (Mitchell et al. 2000), and contains 30–50% CaO (Eger and Mitchell 2007). In cells identical to those described for their UNR-KP study,

Table 1 Cumulative pH and percent reductions in masses of iron and sulfate released from silicate and phosphate coating treatments as compared to a limestone-only surrogate control (Vandiviere and Evangelou 1998)

Sample	Treatment	pH	Fe	SO_4
Tailings with 113% Neutralization (over 28 months)	$CaCO_3$ only	6.6 ± 0.09		
	30 mg/L Si	7.5 ± 0	≈68% ± 12%	≈ -2% ± 10%*
	150 mg/L Si	7.1 ± 0.05	≈51% ± 21%	≈ -4% ± 10%*
	300 mg/L Si	7.1 ± 0.05	≈71% ± 12%	≈ -5% ± 10%*
	30 mg/L P	7.1 ± 0.05	≈67% ± 13%	≈2% ± 11%
	300 mg/L P	7.1 ± 0.05	≈70% ± 12%	≈ -11% ± 11%*
	3,000 mg/L P	6.4 ± 0.4	≈60% ± 20%	≈23% ± 11%
Tailings with 9% Neutralization (over 18 months)	$CaCO_3$ only	1.7 ± 0.03		
	30 mg/L Si	1.9 ± 0.08	≈61% ± 24%	≈52% ± 18%
	150 mg/L Si	1.9 ± 0.01	≈59% ± 9.0%	≈50% ± 6%
	300 mg/L Si	1.9 ± 0.05	≈66% ± 18%	≈53% ± 12%
	30 mg/L P	1.9 ± 0.02	≈37% ± 6.9%	≈36% ± 7.5%
	300 mg/L P	1.8 ± 0.06	≈6% ± 6%	≈8% ± 5%
	3,000 mg/L P	1.8 ± 0.04	≈34% ± 22%	≈15% ± 5.3%
Coal Spoil with 9% Neutralization (over 19 months)	$CaCO_3$ only	2.1 ± 0		
	150 mg/L Si	4.9 ± 2.7	≈80% ± 75%	≈49% ± 24%
	300 mg/L Si	2.1 ± 0	≈ -7.2% ± 64%*	≈12% ± 22%
	300 mg/L P	2.1 ± 0.1	≈ -124% ± 151%*	≈ -42% ± 57%*
	3,000 mg/L P	4.6 ± 2.4	≈26% ± 94%	≈24% ± 36%

* Negative sign indicates treatment concentration was higher than untreated unit

Trudnowski and Lewis (2004) treated waste rock by spraying it with an aqueous solution of ≈ 0.0060 kg KB-SEA™/kg rock (12 lb/ton) after each ≈ 0.3 m lift was loaded into the duplicate cells and monitored leachate from precipitation. During the first 7 months (2001), the leachate pH from the treated cells ranged from ≈ 6 to 7.92, but then dropped to ≈ 2–3 in samples collected in 2002. Control leachate pH ranged from ≈ 2 to ≈ 6.5 in 2001 and dropped to ≈ 2 to ≈ 4 in 2002. Except for two sampling dates, dissolved As concentrations remained below the discharge limit of 190 µg/L, while leachate concentrations from the control units ranged from ≈ 8 µg/L to ≈ 200 mg/L. Dissolved Zn concentrations leached from the treated cells ranged from ≈ 100 ug/L to ≈ 20 mg/L, which exceeded the discharge limit of 338 µg/L on all but one sampling date. Average percent reductions in dissolved concentrations over the 20 months were reported as 88.14% ± 29.25% (Al), 94.82% ± 14.44% (Fe), and 33.18% ± 132.07% (SO_4) (Trudnowski and Lewis 2004).

After removing and stockpiling 301 mm of overlying material, Mitchell and Anderson (2000) treated a 305 mm depth of a 23 m^2 area of tailings-impacted sediment at the Cataldo Flats site in the Coeur d'Alene River Basin (ID, USA) with KB-SEA™ by physically mixing it into the layer, followed by adding a small amount of water to activate the coating. The authors replaced the stockpiled material and after ≈ 1 mo, they obtained solid samples from the treated depth (305–610 mm) for toxicity characteristic leaching procedure (TCLP) analysis by two laboratories. Concentrations from the treated material were 0.31 mg/L Cd (both labs), 5.91 mg/L and 17.01 mg/L Pb, and 23.37 mg/L and 22.28 mg/L Zn; pH was 12 and 12.03. The TCLP was also conducted on untreated material at one lab and concentrations were 0.34 mg/L Cd, 31.37 mg/L Pb, and 34.76 mg/L Zn and the pH was 6.8. The synthetic precipitation leaching procedure (SPLP) was conducted on treated material, but not on untreated material. Concentrations measured in the SPLP for the treated material were 0.004 mg/L Cd, 1.24 mg/L Pb, and 0.35 mg/L Zn and the pH was 12.0 (Mitchell and Anderson 2000).

Laboratory

Eger and Mitchell (2007) conducted duplicate HC tests for 318 wks on 1 kg samples of washed, crushed (0.021–0.64 cm) unoxidized waste rock that had been treated with KB-SEA™ by flooding the columns and then draining them after 10 min. The cells were leached weekly by a slow drip of deionized (DI) water. The initial pH in effluent from the treated cells was 12 or higher, which decreased slowly over time to 4 (1% KB-SEA™), 7.5 (3% KB-SEA™), and 7.8 (5% KB-SEA™) at 318 wks. The initial pH values in the control cells (0% KB-SEA™), were 5.6 and 6.55 and decreased quickly to stabilize at an average of ≈ 3.3 after 19 wks. Only one control was monitored longer than 60 wks. Average percent reductions in sulfate concentrations at 318 wks were ≈ 93% (3% and 5% KB-SEA™) and ≈ 50% (1% KB-SEA™). Microprobe analysis of fragments from unleached treated rock showed KB-SEA™ on the surfaces of pyrite and other mineral grains. Analysis of leached treated rock showed that Si was present along the edges of some pyrite grains, that some grains were oxidized while others were not, and that the amount of oxidation visible decreased with increasing treatment concentration (Eger and Mitchell 2007).

Fytas et al. (1999) examined Na_2SiO_3 in the laboratory for 80 days (d) on unoxidized fresh tailings using different combinations and amounts of Na_2SiO_3, NaOAc, hydrogen peroxide (H_2O_2), $CaCO_3$, quartz sand, and tailings in duplicated columns. The control columns contained 200 g tailings and were leached weekly with DI water. One column (Column C) contained 200 g tailings that were treated in two stages with 0.01 M NaOAc and 0.1 M Na_2SiO_3, followed by 0.01 M NaOAc and 0.05 M Na_2SiO_3, and leached weekly with DI water. All of the other columns contained some combination of quartz sand, $CaCO_3$, or a higher mass of tailings. Percent reductions in leached Fe and SO_4 were not presented and could not be calculated for this review because data were not provided for Column C. Scanning electron microscopy (SEM) analysis indicated that about 20% of the pyrite grains in Column C had a partial coating, although the authors did not specify the mineralogy. Leachate data were provided for columns D and E only, which authors stated had the "best results"; these two columns each contained 20.05 g $CaCO_3$ and 371.85 g tailings. For the D and E columns, SEM indicated a coating of sodium silicate precipitate and for columns containing 7 g $CaCO_3$ and 200 g tailings (Columns F, G, and H), SEM indicated about 20–30% of the pyrite was coated with a mixture of precipitated sodium silicate and ferric-hydroxide-silicate (Fytas et al. 1999).

Roy et al. (2020) coated 70 kg neutral waste rock with 0.2 M Na_2SiO_3 both with and without H_2O_2 and sodium bicarbonate ($NaHCO_3$), and found that at 204 d, the leachate had ≈ 0.34 and ≈ 0.37 mg/kg cumulative Fe, respectively, while the untreated and $H_2O_2/NaHCO_3$ treated controls produced ≈ 0.02 and ≈ 0.05 mg/kg cumulative Fe, respectively. Although the cumulative masses of Fe in the leachate from the treated waste rock were higher than from the controls, the cumulative masses of sulfur released were ≈ 60% lower from the silicate-only coated rock compared to the untreated control and ≈ 35% lower from the $Na_2SiO_3/H_2O_2/NaHCO_3$ treated rock than from the $H_2O_2/NaHCO_3$ control. The initial pH of the control was 7 and the pH ranged from ≈ 6.5 to ≈ 8 over time. The leachate pH from the Si-treated rock decreased steadily over time from ≈ 12.5 to ≈ 8.3. SEM analysis showed Si and Al in an iron oxyhydroxide coating on borders of pyrite particles.

Phosphate

Field

To facilitate formation of an iron phosphate (Fe-PO_4) coating on pyrite surfaces, a buffered (preferably between pH 5–7) phosphate (PO_4) solution is used with an oxidizer (Evangelou and Huang 1994). In parallel with their silicate study on tailings and coal spoil, Vandiviere and Evangelou (1998) conducted experiments with monopotassium phosphate (KH_2PO_4, MKP) at concentrations of 30 mg/L P (tailings only), 300 mg/L P, or 3,000 mg/L P; all columns were prepared and treated the same as in their silicate study described previously. Percent reductions were not presented by the authors but were calculated for this review as described in the silicate section and are shown in Table 1.

Mudder et al. (2005) and Olson et al. (2005) applied 60 g SCN/0.91 mt sodium thiocyanate (NaSCN) and 0 wt%, 0.67 wt%, or 0.24 wt% dicalcium phosphate (Dical) to test pits containing ≈ 545 mt of crushed 9.1% pyrite waste rock (< 7.6 cm) and analyzed leachate over 76 d. Control waste rock pits were untreated. Compared to untreated pits, total dissolved solids (TDS), dissolved Zn, and SO_4 were reduced by > 50% in the pits having both NaSCN and Dical treatment (Olson et al. 2005). The SO_4 leaching rates (g/mt/wk) were reduced by 53% (NaSCN only), 68% (0.07 wt% Dical), and 53% (0.24 wt% Dical) (Mudder et al. 2005; Olson et al. 2006) and PO_4 was released in leachate from the 0.24 wt% Dical test pit (Olson et al. 2006). Initially the pH in the treated pits was > 3.0, but at 76 d it had dropped to 2.3 or 2.4 and remained < 2.5 in samples collected from all pits the year following the initial study (Olson et al. 2006).

Mauric and Lottermoser (2011) constructed three 10 m × 10 m × 3 m piles of waste rock (each ≈ 700 mt) comprising sand to boulder sized shale and siltstone. Crushed limestone berms were constructed at the bases of the piles and sloped inward toward center drains for seepage. After irrigating the piles for 4 wks with potable water, the authors applied 150 kg Trifos (Incitec Pivot Ltd.) or phosphorite rock (Duchess deposit, Queensland) to the tops of two piles and the third pile was untreated. Following treatment, all piles were irrigated monthly, with 4,500 L the first month, 2,000 L for the next 6 months, and rainfall provided irrigation during the last 4 months of the 11–month study. Elemental concentrations and pH fluctuated over time in leachate from all piles. At 34–42 wks, pH and dissolved concentrations of Cu, Ni, Pb, Mn, and Zn were similar in leachate from control and treated piles and dissolved SO_4 concentrations were ≈ 40% (phosphorite rock) and ≈ 50% (Trifos) higher from treated piles at 42 wks. Scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM/EDS) indicated no PO_4 coatings were present, although secondary SO_4 minerals were observed (Mauric and Lottermoser 2011).

Kalin and Harris (2005) placed 8.2 kg natural rock phosphate (NPR) atop fresh and weathered, high and low pyrite waste rock in 70 L drums and prepared control (no NPR) drums with each type of mining waste. The drums were placed outside for 989 d and effluent originating from precipitation was monitored over time. Effluent pH from all drums fluctuated over time and at 989 d was ≈ 6.2 from the fresh low pyrite rock (control ≈ 4.7), ≈ 6.1 from the fresh high pyrite rock (control ≈ 2.5), and ≈ 5.2 from the weathered low pyrite rock (control ≈ 3.5). Relative to controls, elemental concentrations in effluents were decreased by ≈ 77–98% (Al), ≈ 17–90% (Cd), ≈ 25–99% (Cu), ≈ 75–92% (Fe), ≈ -29–73% (Mn), ≈ -77–31% (S), and ≈ 29–89% (Zn). Weathered low pyrite waste rock had lower percent reductions than the other two types of rock, except that Fe (≈ 92%) was similar between both the fresh and weathered low pyrite rock. No data were provided for the weathered high pyrite rock (Kalin and Harris 2005). No Fe-PO_4 coating was observed with SEM/EDS; however, an unidentified organic biofilm was present (Kalin et al. 2012).

Envirobond™ is a proprietary PO_4-based technology developed by Metals Treatment Technologies (MT2) that was applied to waste rock in duplicate cells identical to those used for testing previous technologies by Trudnowski and Lewis (2004). Waste rock was sprayed with an aqueous solution containing ≈ 26.6 kg (58.7 lb) Envirobond™, ≈ 0.0018 m^3 50% H_2O_2, (0.47 gal) and ≈ 0.0731 m^3 (19.3 gal) water per ≈ 900 kg (1 ton) of rock. Leachate pH was between 6.5 and 8.8 (discharge limits) from the treated cells over the 20–month study and was ≈ 2–6.5 (2001) and ≈ 2–4 (2002) from control cells. Except for two sampling dates, dissolved Zn concentrations from treated cells remained below the discharge limit of 338 µg/L, while leachate concentrations from the control units were ≈ 5–100 mg/L. Leachate concentrations of dissolved As were 8 mg/L–100 mg/L from treated rock and ≈ 8 µg/L–200 mg/L from the control units. The authors reported that average percent reductions in leachate dissolved concentrations over the 20 months were 99.98% ± 0.03% (Al), 99.99% ± 0.02% (Fe), and − 275.04% ± 723.36% (SO_4). Percent reductions in dissolved SO_4 concentration were negative for all but the last sampling date in 2001 (24.71%), and positive for the two sampling dates in 2002 at 84.91% and 88.37% (Trudnowski and Lewis 2004).

In addition to their MgO and UNR-KP studies, McCloskey and Bless (2005) tested Ecobond™ (MT2), which supersedes MT2's Envirobond™ (Mahoney and Butler 2021).

The soluble PO_4 in Ecobond™ forms a ferric phosphate precipitate that prevents leaching and is designed to react with pyrite within 24–48 h (McCloskey and Bless 2005). MT2 sprayed ≈ 1.1 m^3 (300 gal) Ecobond™ onto a ≈ 15 m × ≈ 15 m section of highwall in several applications and the rinsate was monitored over time. At 13 mo, rinsate pH was 3.5 from the treated highwall and 3.4 from the untreated highwall. Percent reductions in the cumulative total mass loadings per unit area were 20% (Al), -211% (Cu), 24% (Fe), 49% (Mn), 48% (Ni), and −40% (Zn). The time-averaged total SO_4 concentration in rinsate from treated areas was 31% lower than from untreated areas (McCloskey and Bless 2005).

Laboratory

Mauric and Lottermoser (2011) conducted laboratory leaching experiments on homogenized waste rock (2–30 mm) using two sources of phosphorite rock (Duchess deposit and Century Mine) and MKP (Incitec Pivot Ltd.). In one experiment 2 kg waste rock was treated with 54.8 g MKP in 1 L of DI water or 200 g phosphorite rock placed on top; in the other experiment, 1 kg waste rock was treated with 12.5 g MKP in 1 L of DI water or 100 g phosphorite rock placed on top. Each set had an untreated control.

The 2 kg waste rock group was leached weekly for 13 wks with single additions of 400 mL DI water and dried between water additions. The 1 kg waste rock set was leached weekly for 11 wks with single applications of 400 mL H_2O_2 solutions (0.01 M wks 1–5; 0.1 M wks 6–8; and 0.5 M wks 10–11; the authors did not state what was used in wk 9) and dried between applications. While pH and dissolved concentrations of elements varied over time, pH at the end of both experiments was higher (≈ 6 and 6–8 for the MKP and phosphorite rock, respectively) in effluent from treated waste rock than from the controls and Cd, Cu, Ni, Mn, Pb, and Zn concentrations were lower in leachate from treated rock than from the controls. Leached dissolved SO_4 concentrations were higher than the controls for all treatments leached with H_2O_2, but ≈ 5% to ≈ 43% (phosphorite) and ≈ 72% (MKP) lower in all treatments leached with DI water. Secondary PO_4 phases were observed by SEM/EDS only for the waste rock treated with MKP (Mauric and Lottermoser 2011).

Harris and Lottermoser (2006) coated 400 g partially-oxidized, sulfide-rich waste rock (2–10 mm) in columns using two commercial grade PO_4 fertilizers (MKP and Trifos; Incitec Pivot Ltd.) by leaching daily for 13 d with two 200 mL aliquots of solutions containing 0.2 M NaOAc buffered to pH 5, 0.4 M MKP, 100 g Trifos, or 200 g Trifos, and 0 M, 0.1 M, or 0.2 M $KMnO_4$. After leaching the coated and uncoated rock samples for 13 d with daily additions of two 200 mL aliquots of 0.01 M H_2O_2, the leachate dissolved concentration of SO_4 was highest (≈ 20 mg/L) from the 200 g Trifos + 0.1 M $KMnO_4$ coated rock, lowest (≈ 10 mg/L) from the rock treated with 200 g Trifos but no $KMnO_4$, and ≈ 15 mg/L from the other treatments and the control. For all treatments, leachate dissolved concentrations of As and Sb were higher than concentrations leached from the controls and dissolved concentrations of Cu, Pb, and Zn were lower, with the least amount leached from treatments having MKP + $KMnO_4$; pH in leachate from treated columns ranged from 2 to 3 units higher than from controls (Harris and Lottermoser 2006).

Using the same methodology as for their KB-SEA™ study, Eger and Mitchell (2007) coated waste rock with Ecobond-ARD™ (MT2) at concentrations of 0% (controls), 1.5%, 3%, and 4.5% by weight and monitored leachate from HC tests for 60 d. Initial pH in effluent from the treated cells was 8.4–9.06 and decreased to within ≈ 0.2 pH units of the control units (pH 3.3) at 60 wks. SO_4 concentrations in leachate from treated cells ranged from ≈ 40 to ≈ 60 mg/L at 60 wks, which was ≈ 50% lower than from the controls. Initial concentrations of As released from the treated cells ranged from ≈ 0.4 to ≈ 0.8 mg/L, which was ≈ 2 orders of magnitude higher than in leachate from controls. After 8 wks, As concentrations dropped to 10–20 µg/L. Initial phosphorus (P) concentrations ranged from 1.3 g/L to 3.9 g/L, but decreased rapidly, reaching < 0.03 mg/L at 14 wks; concentration in the controls initially ranged from 0.01 mg/L to 0.02 mg/L and was 0.01 mg/L at wk 10. Pyrite grains from unleached treated rock showed a coating of phosphorus and potassium in electron microprobe analysis, but they were not chemically bonded. Leached treated rock had visible oxidation and some evidence of the Ecobond-ARD™ on edges (Eger and Mitchell 2007).

Triplicate HC tests were conducted for 41 wks on highwall rock that was crushed (size ≈ 0.64 cm × ≈ 1.3 cm (0.25 in × 0.50 in) and saturated in the field with Ecobond™ (McCloskey and Bless 2005). At 41 wks, the average pH was 7.22 in leachate from treated rock and 2.81 in leachate from untreated rock. Percent reductions in time-averaged concentrations (mg/kg) were ≈ 99% (Fe) and ≈ 63% (SO_4). Average concentrations of Al, Cu, Fe, and Ni were below their detection limits throughout the 41 wks, while Mn was 0.011 mg/l until week 22 and Zn was 0.025 mg/l until week 10, after which both Mn and Zn were also below their detection limits (McCloskey and Bless 2005).

Envirobond™ ARD (Rocky Mountain Remediation Services, RMRS) is a proprietary formulation of PO_4 and selective additives that reacts with metals (e.g., iron in pyrite) on the surfaces of soils or soil-like waste to form stable, insoluble PO_4 compounds that coat the surface (Gobla et al. 2000; Jensen and Sogue 2000). Gobla et al. (2000) coated waste rock from the Summitville Mine highwall (Summitville, CO) with Envirobond™ ARD both with and without a strong oxidizer (not identified) and analyzed leachate from daily saturation with tap water. After 20 d, leachate pH was ≈ 7 from the coated waste rock, both with and without the oxidizer, and ≈ 3.2 from the untreated rock; the percent reduction in ferrous iron was ≈ 90% (Gobla et al. 2000). The authors also coated two samples of waste rock from the Ponsardine mine dump (Leadville Mining District, CO), with one sample having ≈ 40% sulfide content. After 15 d, the leachate pH from the 40% sulfide rock was ≈ 6 (treated) and ≈ 1 (untreated) and the leachate pH from the other rock sample was ≈ 8 (treated) and 2.2 (untreated) (Gobla et al. 2000).

Polymers

Field

Intermountain Polymers (ID, USA) developed a two-component acid-catalyzed binder, furfuryl alcohol resin sealant (FARS) that produces a stable polymer to coat particles and mitigate leaching that was tested by McCloskey and Bless (2005) on highwall surfaces at the Golden Sunlight Mine (MT, USA). The FARS product was mixed with 2% (v/v) proprietary acid catalyst for each ≈ 0.02 m^3 (5 gal) batch and the solution (pH 4.5; viscosity 1–3 cp.) was spray applied to the ≈ 15 m × ≈ 15 m highwall area at ≈ $6 \times 10^{-4} m^3 s^{-1}$ (10 gpm) by Intermountain Polymers in two ≈ 0.4 m^3 (100 gal) applications, with 1 h stabilization time between applications. After 13 mo, the average pH of rinsate was 4.9 (treated areas) and 3.4 (untreated). Percent reductions in the cumulative total mass loadings per unit treated area were 75% (Al), 85% (Cu), 85% (Fe), 84% (Mn), 90% (Ni) and 91% (Zn), and the time-averaged total SO_4 concentration in rinsate from treated highwall was 89% lower than in rinsate from the untreated wall (McCloskey and Bless 2005).

Laboratory

McCloskey and Bless (2005) conducted triplicate HC tests for 41 wks on highwall rock that had been crushed to ≈ 0.64 cm × ≈ 1.3 cm (0.25 in × 0.50 in) and saturated in the field with FARS. After 41 wks, the average leachate pH was 4.52 (treated) and 2.81(untreated). Between 32 and 41 wks, average leachate concentrations were 3.73 mg/l Fe, 0.54 mg/l Mn, 0.028 mg/l Ni, and 0.21 mg/l Zn, while Al and Cu were below their detection limits. Percent reductions in time-averaged concentrations (mg/kg) were ≈ 24% (Fe) and 79% (SO_4). The authors stated that the material needed to be broken apart, which exposed some untreated rock surfaces during HC testing (McCloskey and Bless 2005).

Discussion

Table 2 (highwall studies), Table 3 (waste rock studies), and Table 4 (tailings and coal spoil studies) provide summaries of study type, study duration, differences in pH, iron, and sulfate (or sulfur when authors provided that instead of sulfate) resulting from treatment relative to untreated materials and note whether studies included surface analysis to verify coating formation. Differences in experimental (e.g. time, application method) and environmental conditions (e.g. temperature, material sizes) preclude a direct comparison between laboratory and field studies of the same technologies on identical or the same general type of mine waste. In general, however, percentage reductions in leached concentrations of Fe and SO_4 were higher in laboratory studies of the same technology on both identical or similar mine waste materials than in field studies, and leachate pH also was generally higher. An exception was the FARS technology, where the hard coating was broken during placement into columns for the laboratory study and therefore areas of rock that were uncoated were exposed during the experiment (McCloskey and Bless 2005).

Differences in study designs among the technologies within mine waste types, whether comparing across the field studies or the laboratory studies, also can be compared only generally. Phosphate-based coatings were the least effective and were observed in both field and laboratory studies to release more Fe and SO_4 than untreated controls. The treatment appearing to have the most success in the field, based on highest percent reduction of both Fe and SO_4, was FARS. The Dupont Technologies patented potassium permanganate technology performed better when applied to waste rock in

Table 2 Summary of studies on highwall surfaces (McCloskey and Bless 2005)

Chemical	Study Location	Duration	pH Unit Difference[1]	% Difference[1] in Fe, SO_4	Coating Presence Examined?
MgO	Field	1 yr	None	+ 16% Fe, 21% SO_4	No
	Lab	41 wks	+ 3.76	99.5% Fe, 73% SO_4	No
Ecobond™ (MT2)	Field	13 mos	0 to + 0.1	24% Fe, 31% SO_4	No
	Lab	41 wks	+ 4.4	≈ 99% Fe, ≈ 63% SO_4	No
Furfuryl alcohol resin sealant (FARS)	Field	13 mos	+ 1.5	85% Fe, 89% SO_4	No
	Lab	41 wks	+ 1.7	≈ 24% Fe, 79% SO_4	No

[1] In comparison to untreated control units, a plus sign indicates an increase

Table 3 Summary of field and lab studies on waste rock

Chemical	Study Location	Duration	pH Unit Difference[1]	% Difference[1] in Fe, SO_4 (or S)	Coating Presence Examined?	Reference
$KMnO_4$-based UNR-KP	Field	20 mos	+ 1.8 to + 3.55	≈ 100% Fe, 73.43% ± 38.58% SO_4	No	Trudnowski and Lewis 2004
Na_2SiO_3	Lab	204 d	+ 0.5 to + 1	+ 1,600 to + 600% Fe, ≈ 60% S	Yes, Si and Al in Fe oxyhydroxide	Roy et al. 2020
Na_2SiO_3 – based KB-SEA™	Field	20 mos	≈ + 4 to ≈ + 5.9 (2001) ≈ 0 to ≈ 1 (2002)	94.82% ± 14.44% Fe, 33.18% ± 132.07% SO_4	No	Trudnowski and Lewis 2004
Na_2SiO_3 – based KB-SEA™	Lab	318 wks	≈ + 4	No Fe data, ≈ 50–93% SO_4	Yes, Si on edges	Eger and Mitchell 2007
$CaHPO_4$ (Dical)	Field	76 d (2004)	+ 0.5	No Fe data, 53–68% SO_4	No	Mudder et al. 2005
$CaHPO_4$ (Dical)	Field	After 1 year (2005)	None	No Fe or SO_4 data	No	Olson et al. 2006
$Ca(H_2PO_4)_2$ (Trifos)	Field	42 wks	None	No Fe data, ≈ 50% SO_4	Yes, no PO_4 coating present	Mauric and Lottermoser 2011
$Ca(H_2PO_4)_2$ (Trifos)	Lab	2 wks	+ 2 to + 3	No Fe data, ≈ +33% to ≈ 33% SO_4	Yes, various metal phosphates	Harris and Lottermoser 2006
Phosphate Rock	Field	42 wks	None	No Fe data, ≈ 40% SO_4	Yes, no PO_4 coating present	Mauric and Lottermoser 2011
Phosphate Rock	Field	989 d	+ 1.5 to + 3.6	≈ 75–92% Fe, ≈ +77–31% S	Yes, biofilm present but no Fe-PO_4	Kalin and Harris 2005
Phosphate Rock	Lab	13 wks	+ 0.8 to + 1.8	No Fe data, ≈ 5–43% SO_4	Yes, no PO_4 coating present	Mauric and Lottermoser 2011
KH_2PO_4 (MKP solution)	Lab	13 wks	≈ + 0.8	No Fe data, ≈ 72% SO_4	Yes, secondary PO_4 phases	Mauric and Lottermoser 2011
KH_2PO_4 (MKP solution)	Lab	2 wks	+ 2 to + 3	No Fe data, ≈ 0% SO_4	Yes, various metal phosphates	Harris and Lottermoser 2006
Ecobond-ARD™ (MT2)	Lab	60 wks	+ 0.2	No Fe data, ≈ 50% SO_4	Yes, non-chemically bound PO_4 and K on edges	Eger and Mitchell 2007
Envirobond™ (MT2)	Field	20 mos	0 to + 6.8	99.99% ± 0.02% Fe, + 275.04% ± 723.36% SO_4	No	Trudnowski and Lewis 2004
Envirobond™ (RMRS)	Lab	20 d	+ 3.8	≈ 90% Fe^{2+}, no SO_4 data	No	Gobla et al. 2000
Envirobond™ (RMRS)	Lab	15 d	+ 5 and + 5.8	No Fe or SO_4 data	No	Gobla et al. 2000

[1] In comparison to untreated control units, a plus sign indicates an increase

piles (Trudnowski and Lewis 2004) than when applied to highwall rock (McCloskey and Bless 2005) in field studies. However, the waste rock piles were created by mixing the rock with both MgO and CaO, while the highwall rock was sprayed with NaOH prior to application of the coating. It is not known what influence the MgO and CaO had on the experimental results, but considering the basic minerals were mixed in with the rock, it is likely they contributed to the more favorable results.

Three of the PO_4 treatments on waste rock showed release of As at concentrations higher than those from untreated controls. Harris and Lottermoser (2006) noted that MKP and Trifos treatments were ineffective at mitigating oxidation of arsenopyrite and that SEM-EDS studies did not detect As associated with any phosphate precipitate. A minor amount of As was released from dissolution of the MKP (Harris and Lottermoser 2006. Arsenic also was either released from the Ecobond-ARD™ (Eger and Mitchell 2007), or the treatment facilitated its release from waste rock minerals. Concentrations of As dropped over time, which may have been due to precipitation or sorption onto positively charged iron oxyhydroxides as the pH also decreased over time, although iron data was not presented and the mechanism was not investigated by the authors.

Many limitations were observed in the studies reviewed, including that most did not examine materials treated for the physical presence of a coating. Surface analysis was not conducted in field or laboratory studies on highwall rock (Table 2), tailings or coal spoil (Table 4). Only two field studies included surface analysis, both of which were

Table 4 Summary of studies on tailings and coal spoil

Chemical	Study Location	Duration	pH Unit Difference[1]	% Difference[1] in Fe, SO_4 (or S)	Coating Presence Examined?
Na_2SiO_3	Field[2]	28 mos	+ 0.5 to + 1	≈ 51% ± 21% to ≈ 71% ± 12% Fe, ≈ + 2% ± 10% to ≈ + 5% ± 10% SO_4	No
Na_2SiO_3	Field[2]	18 mos	+ 0.2	≈ 59% ± 9.0% to ≈ 66% ± 18% Fe, ≈ 50% ± 6% to ≈ 53% ± 12% SO_4	No
Na_2SiO_3	Field[2]	19 mos (coal spoil)	0 to + 2.8	≈ + 7.2% ± 64% to ≈ 80% ± 75% Fe, ≈ 12% ± 22% to ≈ 49% ± 24% SO_4	No
Na_2SiO_3	Lab[3]	80 d	Not presented or able to be calculated	Not presented or able to be calculated	Yes, mineralogy not specified
Na2SiO3 – based KB-SEA™	Field[4]	1 mo	+ 5.2	No Fe or SO_4 data	No
KH_2PO_4 (MKP solution)	Field[2]	28 mos	− 0.2 to + 0.7	≈ 60% ± 20% to ≈ 70% ± 12% Fe, ≈ +11% ± 11% to ≈ 23% ± 11% SO_4	No
KH_2PO_4 (MKP solution)	Field[2]	18 mos	0.1 to + 0.2	≈ 6% ± 6% to ≈ 37% ± 6.9% Fe, ≈ 8% ± 5% to ≈ 36% ± 7.5% SO_4	No
KH_2PO_4 (MKP solution)	Field[2]	19 mos (coal spoil)	0 to + 2.5	≈ + 124% ± 151% to ≈ 26% ± 94% Fe, ≈ +42% ± 57% to ≈ 24% ± 36% SO_4	No

[1] In comparison to untreated control units, a plus sign indicates an increase

[2] Vandiviere and Evangelou 1998

[3] Fytas et al. 1999

[4] Mitchell and Anderson 2000

studies of PO_4-based coatings on waste rock (Table 3) and while phosphate precipitates were observed, neither identified the targeted Fe-PO_4 coating. Of the laboratory studies where authors conducted surface analysis, phosphorus and potassium were present on particle edges from Ecobond-ARD™ (MT2) treatment and silica was found on particle edges from KB-SEA™ treatment and found along with aluminum in iron oxyhydroxide precipitates on particles treated with Na_2SiO_3.

Other limitations likely influenced results presented by authors, some of which were acknowledged while others were not. The McCloskey and Bless (2005) field study suffered from a decrease in control sampling locations and treated locations (MgO study) due to highwall movement (acknowledged by the authors), but it also was not clear in their report whether the rock used in the MgO and UNR-KP laboratory tests was pre-treated with NaOH as in the field studies although the initial pH was reported as 12. The Trudnowski and Lewis (2004) study reported a leachate SO_4 concentration for one of the controls on one sampling date that was three orders of magnitude lower than any other sampling date and used that value in calculations of percent reduction in sulfate for all technologies tested but did not do an outlier analysis or acknowledge the potentially erroneous data. With respect to their Envirobond™ field results, the authors attributed the large negative percent reduction to potential enhanced sulfide oxidation from the H_2O_2 in the treatment solution, but the observation may have been compounded by the potential outlier. If the low control value was in error, average percent reductions in sulfate for all technologies they tested would be higher than those reported by the authors and in this review.

Mitchell and Anderson (2000) assessed performance of KB-SEA™ using the TCLP and SPLP, both of which require tumbling of the solids. The TCLP simulates conditions in a municipal landfill setting and the SPLP simulates leaching from atmospheric precipitation. The authors did not provide data for an untreated sample analyzed using the SPLP, which would more closely represent expected field conditions than would the TCLP. Although, for either method, it is not known what influence the agitation had on the stability of the targeted encapsulation layer in the absence of surface analysis, but performance may have been more favorable had a less disruptive leaching method been used.

In discussing their data, Vandiviere and Evangelou (1998) compared treated columns to control columns that did not account for the influence of $CaCO_3$, although $CaCO_3$ is not noted in the patents as a required component for either technology (Evangelou 1996; Evangelou and Huang 1994). The Vandiviere and Evangelou (1998) study has been cited in several review articles, such as Camenzuli and Gore (2013); Park et al. (2019); Sahoo et al. 2013a); Tu et al. (2022), but the question of the contribution of limestone to the performance of the silicate or phosphate treatments has not been noted. Fytas et al. (1999) concluded that “*a ferric hydroxide-silica coating can be established*” and that “*it* *seems to be a promising technology*". Evangelou's patent (1996), however, indicates that a ferric hydroxide-silicate coating is not desired: "*Hence at a pH above substantially 7, a hydroxyl iron silicate coating results that is more soluble and less resistant to acid attacked* [sic] *and thus, less desirable*." The performance of silicate technology in mitigating leaching in the Fytas (1999) study was not able to be determined because data were not provided for the column (C) having the same amount of material (200 g tailings) as present in the control column. The data the authors presented were stated as the "*best results*", but each of the two columns having data presented also contained $CaCO_3$, and the contribution of the limestone to the results was not discussed (Fytas et al. 1999).

In their study comparing KEECO's KB-SEA™ and MT2's Ecobond-ARD™ products, Eger and Mitchell (2007) dismantled an unleached cell treated with 3% KB-SEA™ and found that 50% of the rock grains were cemented together. They noted that the grains were "*so solid that water flow was obstructed, effectively reducing the total area of sulfides exposed in the cell*" (Eger and Mitchell 2007); however, they did not discuss the implications of this observation on their results. If rock was cemented together in the leached cells, exposure of the surfaces to the leaching solution would have been decreased as compared to the surfaces exposed in the control units, leading to an overestimate of the reductions in concentrations leached from the experiment with KB-SEA™. The manufacturer requested the cells be saturated with the Ecobond-ARD™ product for 24–48 h, but the product was drained after 10 min. In their discussion, Eger and Mitchell (2007) acknowledged that 10 min was not long enough to have produced ferric iron to react with the PO_4, but they concluded that the product did not prevent acidic drainage generation. It is unknown whether the product is incapable of preventing acidic drainage generation or whether the failure of the product was due to the lack of following the manufacturer's recommended exposure time.

Conclusions

Multiple coating technologies have been tested in the laboratory, but few have been tested in the field and the number of field studies on a specific coating is limited. Silicate and phosphate were the most studied coatings in field settings, while FARS and MgO each had only one field study found. Field studies that have been reported indicate various levels of success at mitigating leaching of elements from mining wastes; however, whether favorable performance was due to encapsulation of sulfide mineral grains or another process, such as precipitation or co-precipitation of elements as they were leached, is unknown. For the two field studies where surface analysis was conducted, the desired coating was not observed.

Perhaps the most likely reason for the lack of coating technologies being used in the field is the lack of studies on which to evaluate their effectiveness to merit their use. Within the limited field studies found for this review, none assessed the influence of UV, climate, interactive biological and chemical effects, or time – the longest studies were conducted in barrels in field settings rather than on waste fully exposed to environmental conditions. Other issues identified in the studies and in this review that may contribute to lack of use include lack of confirmed coating formation, insufficient details to replicate studies, difficulty in application, pre-treatment needed to alter pH, lack of laboratory studies on unaltered (i.e. not ground to a specific particle size) weathered waste materials, lack of cost data, and technology vendors or companies who have retired or gone out of business (e.g. Intermountain Polymers – FARS and RMRS – Envirobond™ ARD). It would be helpful to have continuity in a technology's availability; however, it is beyond the scope of this review to suggest how that might be attainable.

Further research is needed on coating technologies in the laboratory using unaltered, naturally weathered field-derived waste materials conducted under different and cyclical temperature, UV, and humidity conditions to enable better scale-up potential. Field tests are more expensive than laboratory tests, but there is a need for more controlled testing of technologies in the field where limitations of site and material conditions can be understood. Longer term studies to understand the longevity of coating stability and effectiveness are needed. Studies should assess coating formation and report conditions that may affect a coating's effectiveness and stability, such as particle size distribution, acid-base accounting, mineralogy, site climate conditions, area or volume of waste treated, and amount of coating used. Reporting costs on a per unit area or volume of waste treated is also needed for each coating tested, in the absence of labor costs that vary depending on location and specific entity conducting the work.

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