

SULFIDE OXIDATION AND CARBONATE NEUTRALISATION IN MINE WASTES GENERATES GLOBALLY SIGNIFICANT CARBON DIOXIDE EMISSIONS

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EXTENDED ABSTRACT

Knowledge of mine waste mineralogy, the chemistry of mine impacted water, and laboratory data on the kinetics of sulfide oxidation and related carbon dioxide production indicate that approximately 80% of global mine wastes are a major but unaccounted source of global carbon dioxide emissions.

Iron sulfide minerals (eg. pyrite) occur in association with most commodity types including precious metals, platinum group elements, base metals, tin, tungsten, molybdenum, cobalt, cadmium, iron, arsenic, antimony, vanadium, uranium, coal (black and brown), graphite, and some nickel, rare earth element and lithium deposits. Even a range of construction / quarrying materials contain pyrite. The pyrite concentration in mine wastes typically ranges from below detection limits to >20 wt.%.

When reactive sulfide minerals such as pyrite are exposed to atmospheric oxygen by excavating them from below the groundwater table and bringing them to the surface, they immediately begin to generate acid which reacts rapidly with other minerals in the rock to generate leachate with elevated acid and/or elevated metals. This leachate is referred to as acid and metalliferous drainage or acid rock drainage (AMD/ARD), widely believed to be the single biggest environmental issue facing the mining sector across the world.

Carbonate minerals are similarly ubiquitous in mineral deposits, with the most common phases including calcite, dolomite, ankerite, siderite, rhodochrosite, and magnesite, with many other complex solid solutions. When water migrates into mine waste materials, acid from sulfide oxidation is mobilised and percolates through carbonate bearing materials, resulting in acid neutralisation and carbon dioxide gas release. Not all carbonate minerals are acid neutralising, but all release carbon dioxide upon dissolution. Siderite and rhodochrosite could potentially be more problematic than other carbonate minerals as neutralisation and initial carbon dioxide release can be followed by hydrolysis of iron and manganese which can generate as much acid as was initially neutralised. If this acid encounters either siderite or rhodochrosite again, then the neutralisation and carbon dioxide release process can continue automatically.

A small proportion of the released carbon dioxide can dissolve in porewater within unsaturated wastes, but most of this soluble component is released during degassing of the water once it escapes the mine wastes. While baseline levels of acid generation and carbon dioxide release from mine wastes will occur, pulses of higher acid generation and carbon dioxide release related to flush events can also be expected.

The most common types of mine wastes are above ground unsaturated waste rock piles, underground unsaturated waste rock in backfilled stopes, and tailings deposits. While most mine wastes contain reactive sulfides and carbonates, large tonnage deposits that are pyrite-free include bauxite, manganese and nickel-laterite types.

Earth Systems has been conducting kinetic testwork on sulfidic and carbonate bearing mine waste materials using the oxygen consumption technique for more than 10 years. These tests currently involve simultaneous measurement of oxygen (consumption) and carbon dioxide (production) in hermetically sealed vessels every few minutes for weeks to months. Testwork has been conducted on waste rock, tailings, ore, wallrock and slag at more than 50 sites. These sites include a broad variety of mineral commodities at various stages of development: pre-feasibility, feasibility, operational, and legacy. Oxygen consumption and carbon dioxide production rates have been examined as a function of material type, sulfide content, sulfide type, carbonate content, particle size, moisture content and oxygen concentration. Testwork to date suggests that oxygen consumption is largely due to sulfide oxidation, not carbon oxidation (based on cumulative $\Delta O_2/\Delta CO_2$ ratios). For the same reason, carbon dioxide production is largely attributed to the dissolution of both acid neutralising and non-acid neutralising carbonate mineral phases, and not carbon oxidation.

Direct laboratory measurements show oxygen consumption rates varying between 0.001-22 mmol O_2 /kg rock/day. Acidity generation rates (based on the pyrite oxidation reaction) from this oxygen consumption data indicates rates ranging from 0.5 g to 420 kg H_2SO_4 /tonne/year. This is equivalent to pyrite oxidation rates (POR) of 0.1-70 wt. % FeS_2 /year. This unit of measurement indicates that as low as 0.1 wt.% and as high as 70 wt.% of all pyrite exposed to atmospheric oxygen will decompose to form sulfuric acid per year. Typical PORs for waste rock storage facilities (above and below ground) range from 4 to 8 wt. % FeS_2 /year. PORs for tailings material can often be five times higher, but sulfide oxidation is strongly diffusion limited to the upper 0.5-5.0 m of most tailings storage facilities, and hence testwork procedures for tailings are now more focussed on quantifying oxygen penetration depths into tailings deposits.

Carbon dioxide generation rates range from 0.001-0.99 mmol CO_2 /kg rock/day, which is equivalent to 16g-16 kg CO_2 /tonne/year. Carbonate dissolution efficiency can be estimated from the cumulative $\Delta O_2/\Delta CO_2$ data during testwork, and this varies significantly, often depending on the moisture content of the waste materials. Higher moisture contents can facilitate an aqueous connection between the acid and base components, thereby enhancing acid neutralisation and carbon dioxide release.

Using the laboratory data to help model the behaviour of different mine wastes show that waste rock domains are the key acid and therefore carbon dioxide sources at many mine sites. Unsurprisingly, the modelling also shows that large-tonnage deposits and sulfide and carbonate enriched deposits (eg. lead-zinc) are the largest generators of acid and carbon dioxide.

Four separate studies estimating global mine waste production were completed from 1996 to 2019. Combining this data suggests that at present there is approximately 1.85 trillion tonnes of mine waste on the planet, and that in 2019 close to 100 billion tonnes of mine waste was generated. Using this mass balance data and (i) an estimate of the proportion of reactive and non-reactive mine wastes world-wide, (ii) an estimate of the proportion of waste rock to tailings materials, (iii) average sulfide contents of various mine wastes, (iv) typical sulfide oxidation

rates for various mine wastes, (v) the proportion of waste rock that is oxidising at any time within a storage facility, (vi) the average oxygen penetration depth within tailings deposits, and (vii) the efficiency of carbonate dissolution in waste rock piles, estimates of acidity generation and carbon dioxide release from mine wastes have been produced.

Based on the above it is estimated that 85-750 Million tonnes of H_2SO_4 acidity is generated annually from globally accumulated sulfidic mine wastes. A good deal of this acidity is neutralised by carbonate minerals. It has been estimated that the mining industry generates 1.9-5.1 billion tonnes of CO_2 annually (mckinsey.com: 2020) from conventional sources. Mine wastes could be generating an additional 1-15 wt. % of these mining related CO_2 emissions. This could represent between 30 and 270 million tonnes of carbon dioxide released from accumulated sulfidic mine wastes globally per year (ie. 0.1-0.7 % of total global anthropogenic emissions of 40 billion tonnes per year). These carbon dioxide emissions are growing as mine wastes accumulate, and existing stockpiles could continue to release carbon dioxide for decades to centuries post mine closure.

Improved management of sulfidic mine wastes using existing methods can simultaneously lower carbon dioxide emissions and retard the generation of AMD. Mining companies dedicated to lowering their carbon footprint need to be more strongly focussed on managing sulfide and carbonate bearing waste. While water treatment (in perpetuity) can be used to address water quality impacts, it exacerbates carbon dioxide emissions into the future (from the wastes, the manufacture of reagents, and the long-term energy consumption from plant operation).

The above assessment indicates that responsible resource companies need to consider the direct release of CO_2 from mine wastes and the indirect release of CO_2 from water treatment as significant components of their current emissions. Improved management of AMD generating processes globally is needed to reduce this newly recognised component of the corporate CO_2 emissions footprint from mining.