

## Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material

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**Abstract** Iron-Rich Material (IRM) is the residue from processing electric arc furnace dust, and is an inexpensive passive water treatment medium for metal contaminants. IRM contains iron and akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) which provide high amounts of the properties required for removal of metal contaminants: alkalinity, cation exchange capacity, adsorptive capacity, porosity, surface area, strength, and permeability. IRM can treat water with up to 1 g/L of metal contaminants, can remove to 10 % of its weight in metals, and can be regenerated, reprocessed, or disposed of when exhausted. This paper describes the chemistry, action, capabilities, performance, and design of IRM water treatment systems.

**Keywords** low cost, passive, treatment, mine water, iron-rich material, IRM, acid rock drainage, metal contaminants, lead, copper, zinc, cadmium, nickel, arsenic.

### Introduction

Iron Rich Material (IRM) is a by-product of the removal of zinc from either zinc ore concentrate or zinc-containing waste material, principally generated by the steel industry as electric arc furnace dust. The process takes the zinc-containing material, adds coke and lime, and roasts the mixture in a Waelz Furnace at 1,200 °C to convert the volatile zinc into the gas phase where it is captured for sale. The zinc-depleted residue is known as "Iron Rich Material" (IRM), which has been marketed in the United States under the trade names of "HiSorb" and "Ecotite™" and in Spain under the brand name Ferrosita®.

Potential global IRM production is substantial. Approximately 10–20 kg of EAF dust is generated per tonne of EAF steel produced. Annual world production of EAF steel is currently 500 Mt (Rao 2011), creating a potential world-wide production of 5–10 Mt of IRM per year, so this material is abundantly available world-wide.

### Iron Rich Material

A detailed evaluation of IRM with respect to its use as a water treatment agent has been con-

ducted by one of the US producers, Horsehead Industries (Ramesh 1992; Connors 1994; Gao 1995; Gao *et al.* 1995). The physical properties of run-of-process IRM are summarized in Table 1 and typical examples of chemical composition of IRM are shown on Table 2.

The mineralogy of IRM is complex: stoichiometric analysis, X-ray diffraction, scanning electron microscopy, and electron microprobe analysis has allowed identification and determination of the abundance of the two active components in IRM: iron compounds and akermanite (Table 3). Iron was identified in the form of  $\alpha$ -Iron, Wustite ( $\text{FeO}$ ), Hematite ( $\text{Fe}_2\text{O}_3$ ), and Magnetite ( $\text{Fe}_3\text{O}_4$ ).

As can be seen from Table 2 and Table 3, the composition of IRM is variable; this is the result of the diverse sources of the raw mate-

Parameter	Value	Unit
Surface Area	9.7	m <sup>2</sup> /g
Pore Volume	25	%
Void Volume	41.2	%
Bulk Density	1.5	g/mL
True Density	3.5	g/mL

Source: Gao, 1995, Table 3-1

**Table 1** Physical characteristics of IRM

Element	Palmerton, PA <sup>1</sup>	Calumet, IL <sup>2</sup>
Fe	28.20 %	41.70 %
Ca	10.70 %	7.44 %
Si	8.40 %	n.a.
Zn	4.10 %	1.36 %
Mn	3.60 %	3.47 %
Al	3.60 %	0.30 %
Mg	1.60 %	3.75 %
Cu	0.62 %	0.31 %
Na	0.55 %	0.28 %
Cr	0.31 %	n.a.
K	0.31 %	0.07 %
Pb	0.18 %	0.03 %
Ti	0.17 %	n.a.
Ni	0.12 %	0.06 %
O	36.44 %	n.a.
S	1.10 %	0.18 %

<sup>1</sup>Source: Gao, 1995, Table 3.2; <sup>2</sup>Source: This study; “n.a.” indicates not analyzed

**Table 2** Chemical composition of US-produced IRM

Phase	Formula	Palmerton, PA	Calumet, IL
Iron Oxides	FeO <sub>x</sub> (x = 0–1.5)	36 %	54 %
Akermanite	Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	18 %	25 %

Source: Calculated from Table 2

**Table 3** Mineral composition of IRM

rials that are used in its production, and the differing configurations and operations of Waelz furnaces.

**Mode of operation of IRM as a treatment medium**

The mode of operation of IRM when acting as a treatment medium for metals in wastewater is described by Gao (1995) as follows:

“Every single IRM particle essentially contains ferrihydrite along with a crystalline silicate phase, akermanite, in close proximity (in the order of 100 Å) to one another. Akermanite (calcium magnesium silicate) has a unique ability to produce hydroxyl ions through incongruent hydrolysis reaction without being washed out from the fixed bed. The si-

multaneous presence of akermanite and ferrihydrite in a single particle has a synergistic effect on the sorption process: while akermanite helps neutralize aqueous-phase hydrogen ions (thus enhancing sorption capacity of ferrihydrite), neighboring sorption sites in ferrihydrite quickly remove dissolved heavy metals” (Gao 1995, 8–1).

**Metal removal by IRM**

The ability of IRM to remove metal constituents from wastewater has been investigated by passing water containing metals through test columns containing IRM (Gao 1995; Gao *et al.* 1995), and by observation of wastewater treatment during testing and use of IRM (this study). The experience of the effectiveness of metal removal by IRM is summarized in Table 4.

The removal capacity has been found to be dependent on the contact time between the wastewater and the IRM for both zinc and lead removal: the longer the contact time the greater the uptake capacity of IRM for metals (Table 5). The uptake capacity of IRM is also a weak function of the concentration of the metal in the wastewater (Table 6).

The metal uptake capacity of IRM in the research is supported by testing performed for this study by applying high concentration zinc (chloride) to IRM. Loading of zinc on coarse IRM of 5.2 % by weight was achieved, and additional uptake was available. It is estimated that for high wastewater metal concentrations (>1.5 meq/L) metal loading of up to 10 % by weight of IRM is achievable.

**Quality of discharge from IRM treatment**

The effluent quality resulting from properly designed treatment of wastewater by IRM is in general as follows prior to exhaustion of the treatment capacity of the IRM:

- Divalent metals lead, copper, zinc, nickel, and cadmium are essentially removed.

(semi)-Metal	Removal Effectiveness	Effluent (mg/L)	Capacity (% wt of IRM)	Comment	Reference
Pb	v. Effective	0.001	> 5	Primary target	Gao (1995)
Cu	v. Effective	0.01	> 5	Primary target	Gao (1995)
Zn	Effective	0.02	> 5	Primary target	Gao (1995)
Ni	Effective	0.005	Unknown	Primary target	Gao (1995)
Cd	Effective	0.001	> 5	Primary target	Gao (1995)
Fe	Effective	0.1	> 5	Capacity estimated <sup>1</sup>	This study
Mn	Effective	0.01	> 5	Capacity estimated <sup>1</sup>	This study
As	Effective	0.01	Unknown	Capacity not reached	This study
Se	Limited	0.02	Likely limited	High solubility	This study
Ag	Unknown			Untested <sup>2</sup>	
Al	Unknown			Untested <sup>2</sup>	
Ba	Unknown			Insoluble sulfate	
Hg	Unknown			Low solubility	
Mo	Unknown	0.05	Released by IRM		Gao (1995)

<sup>1</sup>Estimate assuming divalent form capacity similar to zinc; <sup>2</sup>Ag, Al concentrations in test liquors too low to allow evaluation of removal effectiveness or capacity; v.: very

**Table 4** Metal treatment effectiveness of IRM

Contact Time	1 min	10 min	1 h	1 d	1 week
Metal Removal (wt % of IRM)	1.2	2.7	3.9	5.9	7.2

Source: Data from Gao (1995), for lead at 0.145 meq/L in influent.

**Table 5** Metal removal capacity of IRM vs. contact time

Influent Zinc Concentration	mg/L	3	6	15	30
IRM Zinc removal capacity	% by wt	0.9	1.0	1.1	1.3

Source: Data from Gao (1995), for zinc with contact time = 1 min

**Table 6** Metal removal capacity of IRM vs. influent metal concentration

- Multivalent iron, manganese and selenium are partially or totally removed.
- Arsenic is partially removed
- Mineral acidity is removed.
- Calcium and magnesium are generally unchanged or are increased by dissolution or ion exchange, but can also be partially removed by precipitation as gypsum, calcite, or dolomite.
- pH is elevated, to between 8 and 12 depending on age of the IRM and contact time
- Sulfate and other non-metallic influent constituents essentially unchanged.

The quality of discharge from typical IRM treatment of an ARD-sourced wastewater is illustrated in Table 7, using data from

a large scale vat test of IRM conducted for this study.

#### Ecotoxicity of effluent from IRM treatment

Samples of effluent from treatment of ARD-sourced water have been evaluated for ecotoxicity for two standard indicator species (Table 8). The tests indicate that the two standard indicator species can survive in essentially undiluted IRM, showing that the effluent is generally benign to aquatic life.

#### Hydraulics of IRM during wastewater treatment

The hydraulic conductivity of intact IRM was measured in this study, and was found to range from  $5 \times 10^{-6}$  to  $5 \times 10^{-8}$  m/s. These values are sufficient to allow flow through the

Field Parameters	Influent	Effluent
pH	5.9	10.6
Conductivity (µS/cm)	3070	2830
Temperature (°C)	14.1	14.6
Major Ions (mg/L) and parameters		
TDS	5230	4300
SO <sub>4</sub>	3190	2780
Cl	31	36
Ca	300	670
Mg	410	170
(semi)-Metals (mg/L)		
As	0.150	0.009
Cd	0.006	0.001
Cr	0.005	0.005
Fe	290.000	0.090
Mn	150.000	0.008
Mo	0.003	0.044
Ni	0.068	0.003
Se	0.086	0.013
Zn	41.000	0.022

**Table 7** Typical treatment of ARD-sourced water by IRM

particles of IRM, and the high porosity of the particles (Table 1) also allows ready access for diffusion within the particles.

Granular IRM has a high inherent permeability, in the order of  $5 \times 10^{-4}$  to  $5 \times 10^{-2}$  m/s, varying considerably between different production locations and batches of IRM. This hydraulic conductivity is typical of a coarse sand and gravel, which is consistent with the appearance and measured grainsize distribution of the IRM.

Hydraulic conductivity can be affected by the physical and chemical effects of the water treatment process:

1. Capture of iron hydroxide particulates formed by oxidation of the influent water by filtration (can cause plugging of pore volume).
2. Precipitation of metal hydroxides formed within the IRM during treatment onto the IRM matrix (reduces pore volume).
3. Changes in volume of the IRM caused by ion exchange between the wastewater and

	Water Flea <i>Daphnia magna</i>	Fathead Minnow <i>Pimephales promelas</i>
48-hour LC <sub>50</sub> , % of IRM effluent	> 100	94

**Table 8** Ecotoxicity testing of effluent from IRM treatment of ARD-sourced water

the IRM (can result in an increase or a decrease in pore volume).

4. Changes in volume of the pore space in the IRM by adsorption of metals from the influent (can cause a decrease in the pore volume).
5. Precipitation of over-saturated compounds due to treatment; particularly precipitation of gypsum due to increase in calcium concentration by ion exchange.

Testing of the treatment process indicates that the cumulative effect of all these processes has the effect of reducing hydraulic conductivity of the IRM as shown in Table 9.

These changes in hydraulic conductivity resulted in each case in an increase in head loss through the IRM treatment medium of less than 0.1 m; the reduction in permeability had no significant impact on the effectiveness of the testing system.

**Performance of an actual passive IRM treatment facility**

The first major application of IRM for water treatment at a metal processing facility in the United States occurred at the Palmerton Zinc Cinder Bank Superfund Site. A total of 90,000 t of IRM was placed in a constructed trench to bedrock at the downhill toe of portion of a large zinc cinder bank. Since 1979 the IRM has been treating an average of 500 m<sup>3</sup>/d of metal-contaminated mine water. This wastewater stream has been cleaned up as illustrated in Fig. 1, with in excess of 98 % reduction in lead, cadmium, and zinc for more than 30 years. The facility is almost entirely passive, requiring only monthly effluent monitoring since its in-

Test	Hydraulic Conductivity (m/s)			Cause <sup>1</sup>
	Before	After	Change	
Column Test [Connors 1994]	$1.5 \times 10^{-2}$	$9.0 \times 10^{-3}$	-40 %	Iron oxide within column
Column Test [this study]	$2.8 \times 10^{-4}$	$1.4 \times 10^{-4}$	-50 %	Iron oxide precipitate on inlet
Vat Test [this study]	$1.1 \times 10^{-3}$	$5.3 \times 10^{-4}$	-51 %	Iron oxide precipitate on inlet

<sup>1</sup>Reference to "iron oxide" is to ochre-colored precipitate, believed to be hydrated ferrous oxide but not tested.

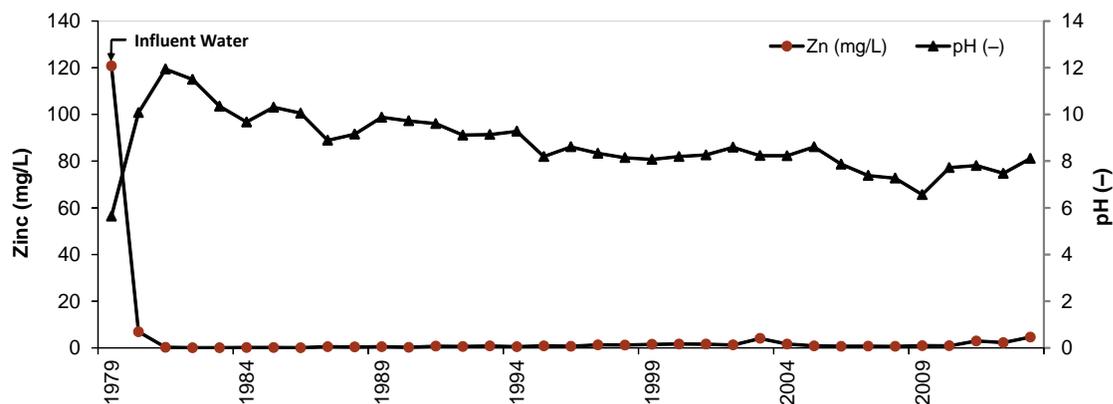
**Table 9** Permeability changes in IRM treatment beds

stallation. To date a total of 768 t of zinc, 1.6 t of lead, and 1.8 t of cadmium have been captured by the IRM in the trench, representing 0.76 % of the IRM mass in the trench.

### Design methodology

The design of an IRM treatment system for a specific site comprises four elements, as follows:

1. Check that IRM can remove the metal contaminants in the wastewater stream. The ability of IRM to remove the metal contaminants in the wastewater can be preliminarily checked by reference to Table 4. For substantial applications of the technology, proof of applicability by direct testing using the actual wastewater is recommended.
2. Check that the concentration of metal contaminants is suitable for IRM treatment. The applicability of IRM as a treatment medium is limited to wastewaters where the concentration of metals is sufficiently low to avoid plugging of the medium by (particularly) gypsum precipitation. During treatment, calcium is released from akermanite by dissolution and ion exchange, which can lead to supersaturation and precipitation of gypsum. A working rule of thumb is that if the total metal contaminant concentration exceeds 1 g/L and the total sulfate concentration exceeds 1.5 g/L in the wastewater, a geochemical as well as bench test check of the possibility of plugging of the IRM treatment medium by precipitation should be conducted before proceeding.
3. Determine the required quantity of IRM for treatment of the wastewater stream. The total mass of metal contaminant that is required to be removed is computed from the known flow rate, the metal concentration(s), and the desired treatment period. The required IRM mass to achieve that removal is computed by assuming



**Fig. 1** Effluent from long-term performance of an IRM mine water treatment system

that it will take up a minimum of 5 % of its weight in total metal contaminants. Bench scale testing of the uptake should be conducted using the actual wastewater stream and the actual IRM which will be used, to verify this computation.

4. Determine the required quantity of IRM to obtain the design contact time. The default retention or contact time is 1 day, which corresponds to the 5 % uptake performance (Table 5). The quantity of IRM that is required to provide sufficient porosity to achieve that retention or contact time can be computed using the measured porosity and density of the IRM, or the values presented in Table 1 above.

A balanced design may be achieved by adjusting the contact time so that quantity of IRM just provides the required uptake capacity and the required retention volume.

### IRM treatment systems

IRM wastewater treatment systems have the following components:

1. Gathering System. Wastewater to be treated is collected and piped to the IRM treatment facility. Where possible, this should be conducted anaerobically to avoid the need to pre-filter the input stream to remove oxidized iron and manganese precipitates.
2. Input. An input zone is generally required for introduction of the treatment water to the system. This is usually a permeable, inert material, such as gravel, separated from the downstream IRM by a geotextile or other permeable medium. If the influent wastewater contains particulates, the input system should be designed to remove them prior to the water entering the IRM. As the methodology is intended to be passive, the filtration should also be passive where possible.
3. Treatment. The wastewater should pass through a relatively long and narrow IRM

pathway, enclosed within a concrete- or synthetic membrane-lined cell from which oxygen is excluded. This approach creates serial treatment, so that the IRM close to the entry point is subject to the highest concentration of metal contaminants in the influent stream, and thus achieves the maximal uptake amount (approaching 10 % of metal by weight in the IRM). The downstream portion of the IRM serves as a polishing area, ensuring that the metal contaminant concentrations in the effluent water meet relevant and applicable discharge standards.

4. Discharge. Treated water should be discharged to contact the atmosphere, preferably in a cascade and/or a wetland. This will result in aeration which will satisfy any oxygen demand prior to release to a surface stream. Incomplete iron and manganese removal may result in some precipitation in this area. In some jurisdictions, it may be necessary to adjust the pH of the effluent water to meet discharge standards, which often require an upper bound pH of 9. This is most easily and sustainably achieved by blending the effluent with equal parts of stream water.
5. Waste disposal. One of the key benefits of IRM treatment systems is that they do not require waste disposal. Properly designed, the wastewater source will in general be depleted before the IRM uptake capacity is exhausted. In the event that this is not achieved, the spent IRM may be either removed for non-hazardous disposal, regenerated using ammonia (Gao 1995), or reprocessed in a Waelz furnace and the metal content recovered.

### Conclusion

Iron Rich Material is an abundant, low cost recycled material which is ideal for passive removal of metal contaminants from mine water and other wastewater streams. IRM comprises an alkaline source in conjunction with an ion exchange medium and adsorptive iron

substrate, in a structurally sound, high permeability, high surface area material. It has the ability to uptake as much as 10 % by weight of metal contaminants. In application, the treatment medium is generally enclosed to maintain anaerobic conditions, and serial treatment removes essentially all metal contaminants from the wastewater stream. It provides a reliable treatment system, which requires only remote monitoring for most operational applications, and does not in general require filtration or waste disposal.

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