Use of sample color to estimate oxidized Fe content in mine waste rock

M. Shum · L.M. Lavkulich

Abstract Color, a readily perceived feature of natural earth materials, including mine waste, often represents compositional variation as a result of oxidative processes involving Fe. Near surface samples from excavated trenches in a mine-waste rock pile were collected to investigate the relationship between color and contents of Fe, Cu, and S. The silt + clay fraction (<0.05 mm) was isolated from recognizable colored material of the bulk sample for determination of pH, total and extractable Fe and Cu, and bulk mineralogy. Rock fragments within the pile exhibited coatings of crystalline gypsum and amorphous Fe. These coatings result from weathering (secondary products) and play important roles in surface reactions of waste rock piles, such as adsorption of anions ($\mathrm{SO_4^{2-}}$) or coprecipitation of Fe with Cu. The correlation between color (Hurst method) and extractable Fe was high. Although color is influenced by site conditions such as original mineral composition, materials handling, weathering conditions etc., the results suggest that color measurements may provide an inexpensive and rapid estimation for secondary iron compounds and associated sorbed elements.

Key words Mine waste weathering · Coatings · Secondary weathering products · Color · Visual estimation

Introduction

A common feature of weathering processes occurring in sulfide containing (pyrite $\mathrm{FeS_2}$, pyrrhotite $\mathrm{Fe_{1-x}S}$, chalcopyrite $\mathrm{CuFeS_2}$) waste rock piles is the formation of a complex assemblage of secondary minerals. The products of weathering are formed by a combination of complex processes including evaporation and $\mathrm{Fe^{II}}$ oxidation (Alpers and others 1994; Nordstrom 1982). During the initial stages of sulfide oxidation, hydrated Fe sulfate minerals (e.g. melanterite $\mathrm{Fe^{II}SO_4\cdot 7H_2O}$) are first to precipitate but continued oxidizing conditions leads to the formation of less soluble secondary Fe minerals (e.g. jarosite $\mathrm{KFe_3^{III}(SO_4)_2(OH)_2}$; Nordstrom 1982).

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The most abundant secondary minerals in this environment are secondary oxides, oxyhydroxides, and sulfates of Fe (e.g. melanterite $\mathrm{Fe^{II}SO_4\cdot 7H_2O}$, copiapite $\mathrm{Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2\cdot 20H_2O}$, goethite α-FeO(OH), lepidocrocite γ-FeO(OH), schwertmannite $\mathrm{Fe_8O_8(OH)_6SO_4}$, jarosite $\mathrm{KFe_3^{III}(SO_4)_2(OH)_2}$; Lin and Herbert 1997; Alpers and others 1994). Unlike typical weathering systems (outcrops, soils), sulfate phases tend to be prominent in the sulfide weathering environment.

Secondary weathering products, especially oxidized Fe phases (goethite, jarosite), can be considered a sink for mobilized elements (Al, Cu, Ni, etc.; Levy and others 1997; Lin and Herbert 1997; Herbert 1995), but activities altering microsite geochemical conditions could lead to the dissolution of some secondary phases and the mobilization of trace elements (Schulin and others 1995; Alpers and others 1994). Thus secondary weathering products can be considered meta-stable and may be an important factor in seepage contaminant loading from waste rock piles.

Of the elements released in weathering environments, Fe is retained most significantly (Schwertmann and Fitzpatrick 1992; Schwertmann and Taylor 1989). Because of its tendency to oxidize and precipitate (as oxides and oxyhydroxides) and its inherent strong pigmentation, oxidized Fe content may be useful as an field indicator of weathering intensity, the accumulation of secondary weathering products, and valuable as a guide for sampling waste rock materials. Recognition of the type and amount of Fe oxides/oxyhydroxides can be useful indicators of the past geochemical environment (Murad and others 1994; Schwertmann 1993; Bigham and others 1990).

Several authors have identified relationships between color with the amount of Fe or type of Fe (mineralogical phase) present. Schoeneberger and others (1992) identified four color zones (red, yellow, white, black), associated with fractures in saprolites, relating to the Fe content and mineralogy. Alpers and Brimhall (1989) used sample dry scratch color for mineralogical identification of limonite minerals. Hurst (1977) suggested visual estimation of total Fe in subtropical and tropical saprolites by using calibration curves developed from either ochre and quartz or hematite and quartz mixtures. Specific components of color were examined (hue, value, and chroma) and then related to total Fe content, particle size, and hydration state of the compounds. The hue was found to be related to the mineralogy and particle size of the ferric pigments; the value and chroma reflected the proportion of the various pigmenting compounds (Hurst 1977). Torrent and others (1983) modified the relationship used by Hurst (1977) to calculate a redness rating in soil samples using visual and spectrophotometric color measurements and found that the redness rating correlated well with hematite content in their samples.

Several selective dissolution analysis techniques have also been used to characterize Fe phases in soils and solids (sediments and precipitates) formed in waters by mine drainage (Karathanasis and Thompson 1995; Bigham and others 1996; Borggaard 1988). Amorphous Fe phases have been extracted using either ethylene diamine tetra-acetic acid (EDTA) or acid ammonium oxalate (AAO) solutions. EDTA solution removes water-soluble and exchangeable, organically complexed, and amorphous or poorly crystalline Fe phases (Borggaard 1988). Oxalate solutions have also been used to dissolve organically complexed Fe and amorphous inorganic Fe, Al, and Si phases from soils (McKeague and Day 1966). Crystalline secondary oxides and hydroxides of Fe can be removed using a dithionite-citrate-bicarbonate (DCB) extraction. The DCB method, considered to be less specific and more aggressive, is used to determine free iron phases, but also removes amorphous coatings and associated elements such as Si, Al, and Mn (Jackson and others 1986; Mehra and Jackson 1960).

Morphology (particle size, color, structure, etc.) has been used as a bias when sampling natural bodies such as in soil (von Steiger and others 1996; Miller and others 1993). Color as determined by the type, particle size, and distribution of Fe oxides is used to explain soil genesis and the degree of weathering and is also an important criteria for naming and classifying soils (Bigham and Ciolkosz 1993; CSSC 1987). Mine waste rock may be considered incipient soils (i.e. similar to natural soil but lacking the organic and biological component) and morphological features (color) commonly used in soil science, may be a useful sampling tool to estimate the degree of weathering. Organic matter in soil strongly influences color, however, in mine waste which has little or no organic matter, color is likely controlled by the amount and type of secondary Fe oxides.

The development of innovative techniques to characterize waste rock composition is an area of important research. Easy and rapid methods to evaluate metal concentration are valuable tools for geochemical mapping of oxidized secondary minerals in mine waste. This paper will examine the relevance of using sample color as a surrogate variable to estimate extractable Fe content in mine waste rock samples, and relationships with other elements (Cu and SO_4^{2-}) which may be coprecipitated.

Materials and methods

Site and sampling description

Gibraltar Mines is an open pit copper-molybdenum mine site in central British Columbia approximately 360-km north of Vancouver (Fig. 1). The Gibraltar property is at an elevation between 914–1231 m on the western flank of Granite Mountain, and receives 32.5-cm precipitation annually. The Gibraltar ore body is a large low-grade porphyritic deposit with copper disseminated in fine-grained igneous intrustions in adjacent host rock (Bysouth and Carpenter 1984). Chalcopyrite ($CuFeS_2$) is the primary Cu mineral mined with minor amounts of molybdenite (MoS_2). The mine has been in operation since 1972.

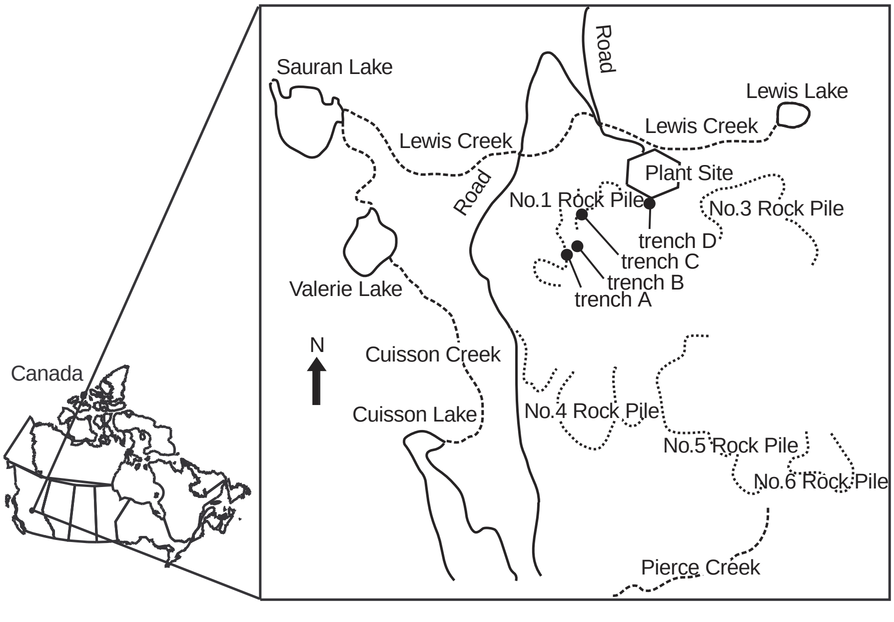

Fig. 1
Site and sampling locations at the Gibraltar mine site

The rock in the waste piles has a relatively uniform mineralogical composition of 50% saussuritized andesine plagioclase, 20% chlorite, and 30% quartz, with plagioclase altered to albite-epidote-zoisite and muscovite. Copper content in the rock dumps varies from 0.11–0.27%, while pyrite rises as high as 3% (Bysouth and Carpenter 1984). There is over 300 million tonnes of waste rock on the site (Feasby and Jones 1994).

Several of the waste rock piles at the Gibraltar Mines have become an important secondary source of Cu. Sulfuric acid is irrigated onto the rock pile surface through a series of irrigation hoses, the leachate is collected in ditches, then pumped to an on-site solvent extraction-electrowinning plant, generating up to 10% of Gibraltar mine's total copper production (approx. 10 tonnes/day; Klohn Leonoff Consulting Engineers 1991).

Four trenches (A, B, C, D), approximately 5-m long × 4-m wide × 3-m deep, were excavated in a variety of different acid-leaching environments on the surface of a 23 million tonnes waste rock pile (Fig. 1). Samples were collected throughout the exposed profile from each trench, stored in sealed plastic bags and transferred to the laboratory for analysis. Samples were collected from morphologically different colored regions of each trench. Samples were selected based on changes in color and particle size.

Analytical procedures

In the laboratory, samples were air-dried, then gently crushed with a wooden rolling pin, and the fine earth fraction (<2 mm), was isolated from the coarse fraction by dry sieving. The fine earth fraction was sieved to isolate the silt + clay (sicl) fraction (<0.05 mm).

The color was determined on the air-dried silt + clay fraction using a Munsell color book (Kollmorgen Corporation 1975) with white paper as a background. The silt + clay fraction was selected because its color is more homogenous than the fine earth fraction. Munsell color descriptions were transformed to a Hurst color rating (Hcr) as described by Hurst (1977). Hurst color rating is calculated from Munsell color notation by using the following relationship:

$$\mathrm{Hcr} = (H^* \times V)/C$$

where: H^* (modified hue) is determined from hue using the conversion below; V and C are equivalent to the numbers from Value and Chroma in the Munsell notation

hue	0R	5R	10R	5YR	10YR	5Y	10Y
H^*	0	5	10	15	20	25	30

e.g. a sample with the Munsell color 10YR 5/6 ($H^*=20$, $V=5$, $C=6$) has an Hcr value of 17 (Hcr = 20*5/6)

Hurst (1977) used this rating system for rapid estimations of the total Fe content in subtropical and tropical saprolites. Higher Hcr values indicate lower Fe content, while low Hcr values indicate greater quantities of Fe. The presence of non-ferric iron containing minerals (e.g. such as melanterite which is blue-green) are likely to have a diluting effect on the intensity of Fe pigmentation resulting in higher Hcr values. For example, Alpers and Brimhall (1989) found that increasing gypsum and silica caused an increase along the value color axis.

Particle size analysis on the fine earth (<2 mm) fraction was determined using the hydrometer method, in combination with sieving to isolate the sand fraction (Gee and Bauder 1986). Samples for particle size analysis were pretreated with DCB to remove cementing agents (Mehra and Jackson 1960).

Analysis consisted of paste pH (1:2 sample:water by mass) using a glass electrode with a Ag/AgCl internal reference and temperature calibration, calibrated at pH 2 and 7. Bulk mineralogy was determined from XRD scans on random powder mounts (samples were crushed in an agate mortar and pestle) using a Phillips, PW 1050/25 diffractometer emitting Cu-K_a radiation ($\lambda = 15.4$ nm). Total Fe and Cu concentrations were measured on samples from XRF analyses conducted on glass (fusion) discs and pressed KBr powder pellets using a computer controlled Phillips 1400 automated X-ray spectrometer (XRF). Total S was determined on a Leco-S (model SC132) analyzer.

Three extraction procedures were used to estimate extractable phases from these samples: (1) amorphous Fe content was determined using acid ammonium oxalate extraction at pH 3 in the absence of light (AAO; McKeague and Day 1966); (2) reducible Fe or total Fe oxide content was determined using a dithionite-citrate extraction buffered to pH 7.3 using bicarbonate (DCB; Jackson and others 1986; Mehra and Jackson 1960); and (3) a 30-min deionized H_2O extraction for water-soluble S (Bayless and Olyphant 1993; Blowes and Jambor 1990). AAO and DCB extractions followed the methods of McKeague and Day (1966) and Mehra and Jackson (1960) as modified by Lavkulich (1982). Solutions from AAO and DCB procedures were isolated by centrifugation at 8000 g for 20 min. Solutions were analyzed for Fe and Cu using an air-acetylene flame, on a Perkin Elmer AAS model 306 instrument. Turbidimetric sulfate was determined following Rhoades (1982).

Statistical relationships were examined with Spearman rank correlation coefficients and regression analysis determined using the SPSS statistical software package (SPSS 1995).

Results and discussion

Field observations

The exposed profiles in the trenches revealed two morphologically different patterns of waste rock material depending on the proximity to the crest or edge of the rock pile. Profiles located in trenches near the crest of the dump showed highly-structured (stratified), steeply-dipping layers defined by changes in color (due to oxidation) and particle size. Deposition of waste rock near the edge of the rock pile likely led to the presence of the layers sloping downwards at approximately the angle of repose. Profiles in trenches away from the dump crest did not have structured layering, but showed random and irregular patterns of oxidation. The four trenches (A, B, C, D), at the time of sampling, had experienced significantly different acid leaching regimes. Trench A and B were located in an area where leaching had occurred initially for 4 years at which time leaching was discontinued, and at the time of sampling had not been acid leached for 2 years. Trench C was in an area under active acid leach at the time of sampling, and had been leached for 4 years prior to sampling. Trench D was located in an area where the rock dump had never been acid leached. Trench A and C were located near the crest of the rock pile.

Morphological characteristics

The results from color and particle size analyses are shown in Table 1. Sample color was diverse ranging from reddish brown to white with corresponding Hurst color ratings ranging from 13 to 100. Low Hcr values result in samples with low H^* (hue) and/or high chroma. Samples with low Hcr values were likely taken from a more intense weathering microenvironment (more oxidizing, greater leaching) than samples with high Hcr values because low Hcr is due to: (1) the presence of pigmenting Fe phases (e.g. goethite, hematite, jarosite, schwertmannite, etc.) which tend to form under oxidizing phases, and (2) oxidizing environments are conducive to the accumulation of pigmenting Fe phases (Schwertmann 1993; Schwertmann and Taylor 1989).

The mass of the sieved fine-earth fraction ranged from 9–32% of the total sample mass, with three exceptions where the fine earth fraction contributed to 43, 58, and 63% of the mass. These results are comparable to previous studies at Canadian mine sites where the fine earth fraction ranged from 0–35% (Price and Kwong 1997; Murray 1977). The proportions of sand, silt, and clay in the fine earth fraction occurred in a narrow range with only slight variation. The percentage of coarse material (>2 mm) varied widely. Variations in particle size for material from waste rock piles can be attributed to difference in the age of the waste rock, methods of blasting and materials handling, variation in the strength and competency of the rock, and weathering (Price and

Table 1
Characterization of morphologic features (color and particle size)

ID			Silt + clay color				Particle size analysis				
	Trench depth		Munsell color			Hurst color rating	Sieveing		Hydrometer method		
		(m)	Hue	Va Chr			% coarse (>2 mm)	% fines (≤2 mm)	% sand	% silt	% clay
1	A	3	2.5 Y	7/4	pale yellow	39	42	58	61	27	12
2	A	2.8	2.5 Y	8/4	pale yellow	45	37	63	52	26	12
3	A	2.5	2.5 Y	7/4	pale yellow	39	71	29	60	31	10
4	A	2	10 YR	6/8	brownish yellow	15	88	12	62	25	14
5	A	1.7	10 YR	6/8	brownish yellow	15	74	26	63	26	12
6	A	1.2	7.5 YR	6/8	reddish yellow	13	83	17	53	34	12
7	A	0.9	2.5 Y	8/4	pale yellow	42	69	31	63	25	12
8	A	0.2	2.5 Y	7/3	pale yellow	53	57	43	67	26	7
9	A		10 YR	8/8	yellow	19	69	31	60	27	13
10	B		2.5 Y	8/3	pale yellow	60	84	16	61	29	10
11	B		2.5 Y	8/6	yellow	30	87	13	57	23	19
15	B		5 Y	8/3	pale yellow	67	91	9	65	20	15
16	B		5 Y	8/2	white	100	80	20	60	23	15
17	B		2.5 Y	7/3	pale yellow	53	68	32	62	27	11
18	C	2.4	5 Y	8/3	pale yellow	63	84	16	67	22	11
19	C	2.3	5 Y	7/2	light gray	88	85	15	67	22	11
20	C	2.1	5 Y	7/3	pale yellow	58	80	20	68	24	9
22	C		2.5 Y	7/2	light gray	79	78	22	59	26	15
23	C	1.7	2.5 Y	7/6	yellow	24	76	24	67	22	11
24	C	1.1	5 Y	7/2	light gray	88	84	16	64	36	13
25	C	1	5 Y	7/4	pale yellow	44	71	29	67	21	12
26	C	0.15	2.5 Y	7/3	pale yellow	53	74	26	61	28	11
27	C		2.5 Y	7/6	yellow	24	79	21	72	18	10
28	D		5 Y	7/3	pale yellow	58	88	12	64	26	11
29	D		5 Y	7/3	pale yellow	58	88	12	64	28	8
30	D		2.5 Y	7/2	light gray	79	81	19	62	27	11
31	D		2.5 Y	7/6	yellow	26	74	26	70	21	9
33	D		5 Y	7/4	pale yellow	44	76	24	67	27	6
34	D		2.5 Y	8/3	pale yellow	60	91	9	65	24	11

Kwong 1997). The period of time waste rock is on the surface of a rock pile is an important weathering factor because of traffic, wetting and drying, and insolation.

Chemical analyses

Prior to chemical analyses, examination of samples under a microscope revealed a variety of weathering products coating the surface of all particles. For instance, crystalline gypsum dispersed on the surfaces of amorphous coatings, was clearly evident in all these samples. After AAO and DCB extraction, grain surfaces appeared free of gypsum and the amorphous coatings.

Paste pH values for samples collected in trenches A through D ranged from 2.6–3.6 ($\bar{x}=2.9$), 2.6–3.0 ($\bar{x}=2.8$), 3.3–6.2 ($\bar{x}=4.4$), and 2.6–4.8 ($\bar{x}=3.9$), respectively. Chemical analyses for total and extractable Fe and Cu are summarized in Table 2. Significant correlation coefficients ($P<0.01$) were calculated between paste pH and extractable Fe (negative correlation), and paste pH and extractable Cu (positive correlation). This suggests that acidic conditions are conducive for the formation of secondary Fe phases but may have resulted in the preferential removal of secondary Cu phases. The former is possible since some oxidized Fe phases tend to precipitate at lower pH and many secondary Fe oxides such as hematite, goethite, and jarosite have very low documented solubility products (pKsp < 10–30; Lindsay 1979). Bigham (1994) suggests that schwertmannite and jarosite (Fe-sulfate oxyhydroxide precipitates) are only present in mine drainage streams with sufficient SO_4^{2-} (>1000 mg/l for schwertmannite and >3000 mg/l for jarosite) and pH values 1.5–4.

High Fe concentrations (total and extractable) reflect abundant quantities of Fe-containing primary minerals and the formation of oxidized Fe phases (such as goethite and jarosite). Generally, extractable Fe_{AAO} and Fe_{DCB} concentrations were highest in areas where acid leaching was discontinued or was still occurring (A>B>C>D), suggesting acid-leaching accelerated weathering processes and when leaching was discontinued, changes in hydrologic and geochemical conditions led to an even greater accumulation of secondary Fe. Iron phases soluble in AAO solutions are schwertmannite, ferrihydrite, and amorphous Fe phases, whereas goethite, hematite, and jarosite are more susceptible to DCB extractions (Bigham and others 1996; Schwertmann and Taylor 1989; Borggaard 1988; Schwertmann and others 1982). XRD scans show very weak peaks indicating the presence of secondary hematite, goethite, and jarosite.

Total and AAO extractable Cu levels in the waste rock samples were highest in areas where acid leaching had not occurred and decreased as the acid leaching increased (D>C>A=B). Total and AAO extractable Cu were approximately 2–20× greater from samples in trenches C and D than those in A and B. This was expected since Cu reserves near trench C were high enough to warrant acid leaching, while areas near trench D were never leached with acid. Most of the Cu in trench C and D was extractable using the AAO procedure, whereas in trench A and B, only 50% of the Cu phases were extractable suggesting that aging of secondary Cu phases led to a more stable form. Cu was preferentially extracted by AAO compared to DCB solutions as a result of increased Cu solubility at the lower pH of the AAO extracting solution.

Total S and water soluble SO_4^{2-}-S results are summarized in Table 3. The proportion of water soluble SO_4^{2-}-S to total S ranges from 24–98%, thus a large proportion of total S is water soluble suggesting there is little remaining pyrite or chalcopyrite. Water soluble SO_4^{2-}-S is closely correlated to total S ($r_s=0.82$, $P<0.00$). Paste pH was weakly correlated to the total S ($r_s=-0.45$, $P<0.05$).

Table 2
Summary of total, acid ammonium oxalate, and dithionite-citrate-bicarbonate extractable Cu and Fe. Values are all presented in mg/g

Trench			Total	AAO	DCB
A	Cu	X	0.67	0.31	0.01
		Range	0.39–1.14	0.20–0.55	0.01–0.03
	Fe	X	61	24	31
		Range	39–88	4–74	12–68
B	Cu	X	0.73	0.39	0.01
		Range	0.37–1.11	0.15–0.51	0.01–0.02
	Fe	X	44	9	17
		Range	37–56	3–18	9–26
C	Cu	X	3.96	4.08	0.03
		Range	1.59–8.11	1.20–8.72	0.02–0.05
	Fe	X	52	8	11
		Range	44–62	1–25	3–23
D	Cu	X	13.99	14.03	0.09
		Range	0.64–35.57	0.48–35.20	0.02–0.17
	Fe	X	47	8	15
		Range	30–70	3–22	6–37

Table 3
Summary of total S and water soluble SO_4^{2-}-S analyses. Values are all presented in g/100 g (%)

Trench		Total S	H_2O-SO_4^{2-}-S
A	X	2.16	0.93
	Range	0.35–5.50	0.19–1.35
B	X	2.10	0.92
	Range	0.28–4.40	0.46–1.25
C	X	1.20	0.72
	Range	0.45–3.97	0.34–1.21
D	X	1.21	0.68
	Range	0.73–2.14	0.28–1.43

Larger total S concentrations in samples collected from non-acid leached areas (i.e. trench D) result from the lack of acid irrigation. Higher total S levels in samples from trench A and B may be due to the formation of S or $SO_4{}^{=}$-S phases, such as jarosite or schwertmannite, both of which tend to precipitate at lower pH values and have low solubility (Bigham and others 1996; Bigham and others 1990). In areas with higher pH and/or frequent leaching activity, there is less S and $SO_4{}^{=}$-S accumulation.

Relationships with color

Oxidized Fe phases are strongly pigmenting and, in a rock pile with little organic matter, they are more prominent than other pigmenting phases. Extraction data indicates an abundance of secondary Fe phases (schwertmannite, ferrihydrite, etc). Data analyses indicate a relationship between Hurst color rating and Fe content. Samples with low Hcr tended to have higher amounts of extractable Fe_{DCB} and Fe_{AAO}. Correlation coefficients ($P<0.05$) calculated for Hcr with Fe_{DCB} ($r_s=-0.81$), Fe_{AAO} ($r_s=-0.74$), and Fe_{total} ($r_s=-0.59$) suggest extractable Fe phases have a greater effect on color (thus Hcr values) than Fe from primary minerals. Total S was correlated ($P<0.05$) to Hcr ($r_s=-0.38$), Fe_{AAO} ($r_s=0.63$) and Fe_{DCB} ($r_s=0.58$), thus samples collected from areas with low Hcr tended to have higher concentrations of $SO_4{}^{2-}$-S, oxalate and oxide Fe indicating accumulations of secondary Fe phases and indicating oxidizing areas in the rock dump. Total S was correlated to extractable Fe suggesting the presence of Fe sulfate phases or adsorbed $SO_4{}^{2-}$ anions. This is consistent with other researchers indicating that the presence of high levels of organic matter and $SO_4{}^{2-}$ may hinder or retard the formation of goethite, while favoring the formation of poorly crystalline ferrihydrite or Fe oxyhydroxysulfates (i.e. schwertmannite; Karathanasis and Thompson 1995; Schwertmann and Taylor 1989; Brady and others 1986). There were no significant relationships between total and extractable Cu with Hcr although Cu was negatively correlated to Fe (for AAO, $r_s=-0.41$; for DCB, $r_s=-0.49$).

Figures 2 and 3 show the scatter relationship between Hcr and extractable Fe with the inverse regression line through the data, with error bars showing ±50% of the theoretical extractable Fe. The regression lines follow the data quite well considering the variability expected based on samples taken by visual (color) criteria. The curve of extractable Fe decreases to a lower limit approaching 3–5 mg Fe/g material with increases in Hcr values. This suggests there is a limit to our ability to discriminate color changes at lower Fe levels. These limits may be extended by using diffuse reflectance spectrophotometers or tristimulus colorimeters to measure color. These instruments have been shown to be strongly correlated with Munsell color measurements (Post and others 1993). Typical Fe oxide colors (7.5R-5YR for hematite, 7.5YR-2.5Y for goethite) can be modified by the dark colors of humic materials and/or Mn oxides, grain size, and the moisture content (Schwertmann 1993; Hurst 1977). Thus,

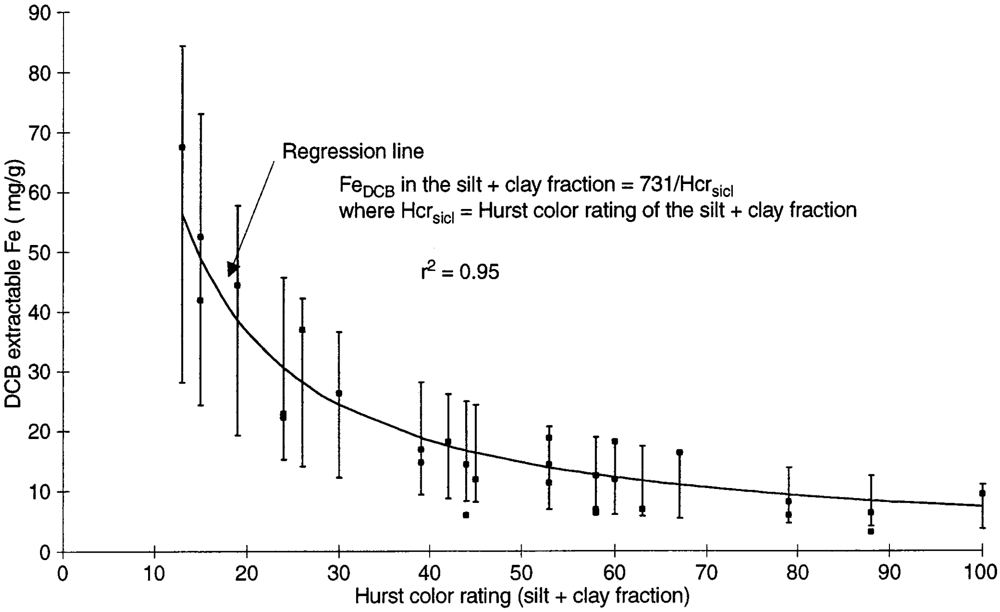

Fig. 2
Dithionite-citrate-bicarbonateextractable iron (Fe_{DCB}) from the silt + clay fraction (< 0.05 mm) vs. Hurst color rating of the silt + clay fraction

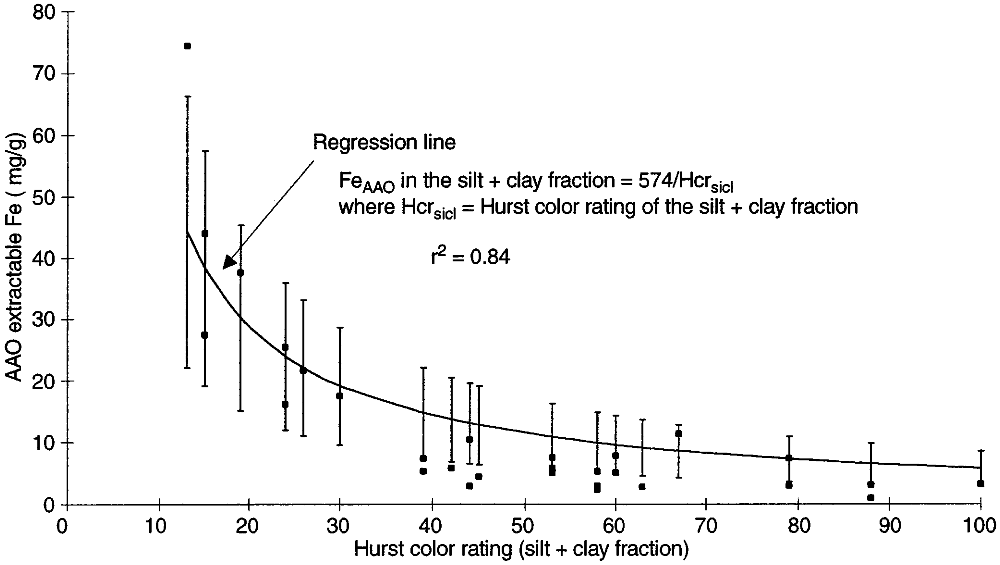

Fig. 3
Acid ammonium oxalate extractable iron (Fe_{AAO}) from the silt + clay fraction (< 0.05 mm) vs. Hurst color rating of the silt + clay fraction

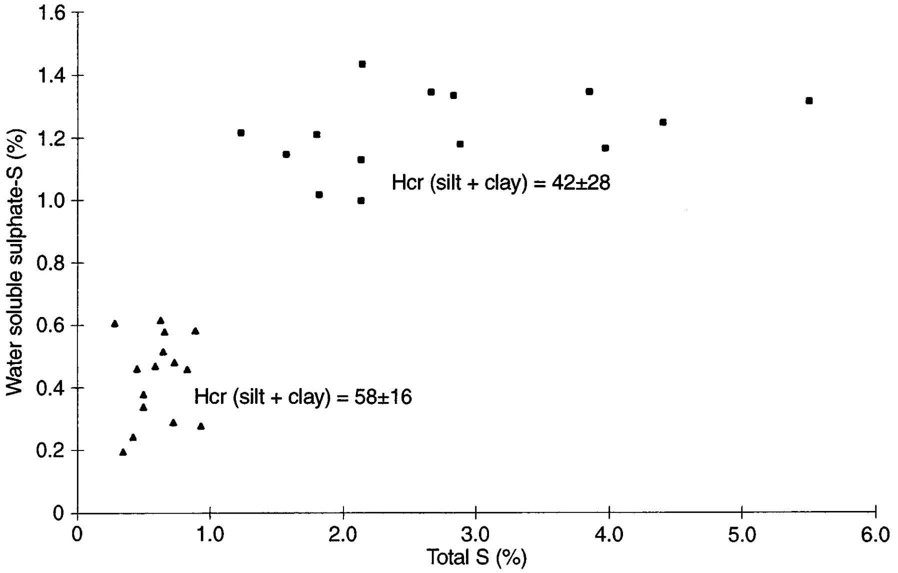

Fig. 4
Water soluble sulfate-S (%) from the silt + clay fraction vs. total S from the silt + clay fraction

variations in Munsell color measurements maybe due to several factors including: (1) moisture content, as this increases value generally decreases, (2) amount, type, and particle size of coloring minerals, and (3) the presence of other coloring agents (organic matter, oxidized manganese phases (Post and others 1993; Hurst 1977). Variations in moisture could be eliminated by determining color on air-dry samples and organic matter pigmentation is not a factor in the rock dump materials.

The oxalate soluble to oxide Fe (Fe_{AAO}/Fe_{DCB}) ratio values appear to be related to sample morphology. As the content of goethite/hematite/jarosite in a sample increases, the values for oxalate soluble to oxide Fe (Fe_{AAO}/Fe_{DCB}) decreases. Samples with $Hcr_{sicl} < 30$ have an average Fe_{AAO}/Fe_{DCB} of 0.89 ± 0.19 and samples with $Hcr_{sicl} > 30$ have an average of 0.47 ± 0.15. Some research has indicated that aging of oxidized Fe phases leads to decreasing Fe_{AAO}/Fe_{DCB} suggesting greater crystallinity (Schwertmann 1993). At this time, the existence of such a relationship in mine wastes is unconfirmed. Values for Fe_{AAO}/Fe_{DCB} increase with decreasing Hurst color rating, suggesting the oxalate soluble phases have a greater pigmenting ability than the oxide component. Bigham and others (1996) found that as the amount of oxalate soluble content increases, there is greater amounts of schwertmannite and ferrihydrite.

Poorly crystalline oxidized Fe phases are likely to have relationships with other metals or anions through coprecipitation and/or sorption mechanisms. A relationship between water soluble SO_4^{2-}-S and total S suggests two distinct populations which is related to the Hcr of the silt + clay fraction (Fig. 4). Samples with lower Hcr (and higher Fe) tend to have higher total S and SO_4^{2-}-S, while those with higher Hcr (low Fe) tend to have lower total S and SO_4^{2-}-S. The higher S and SO_4^{2-}-S levels at lower Hcr values may be due to sorption onto oxidized Fe phases and/or precipitation as a component of an Fe sulfate phase contributing to pigmentation.

Conclusions

Visual estimation using color is a valuable method for researchers and mine operators studying geochemical processes occurring in mine waste from the standpoint of being a quick indicator of accumulated secondary phases and associated elements. Estimation of Fe oxide content could be used as a weathering indicator. Higher extractable Fe contents are typically associated with greater weathering intensities, therefore results indicate relationships exist between color and extractable Fe and S-SO_4^{2-}. The relationship between color and extractable Fe is particularly strong. Low Hurst color ratings were associated with higher extractable Fe and total S. The observed changes appear to be related to changes in the acid leaching regime, and suggest that as leaching ceases, Fe secondary weathering products reorganize into less soluble phases which affects other elements.

The results of this study are specific for this site, however relationships between color and Fe are well documented in the literature. A general relationship needs to be validated by studies at more sites with a range of conditions. Munsell color could be determined in samples collected from mine waste to further delineate relationships which may exist between color rating and elements in secondary products. Use of color as a surrogate variable to obtain field estimates of certain elements could reduce sampling time and costs for mine operators attempting to estimate accumulated weathering products (i.e. geochemical mapping). Estimations may improve by using the silt + clay fraction for visual estimations because the color from this fraction is more uniform, thus reducing the variability.

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