Comparison of color, chemical and mineralogical compositions of mine drainage sediments to pigment

C.S. Kirby · S.M. Decker · N.K. Macander

Abstract Forty-three untreated and actively and passively (wetland) treated coal mine drainage sediments and five yellow-red pigments were characterized using X-ray fluorescence, fusion-inductively coupled plasma atomic emission spectroscopy, X-ray diffraction, and tristimulus colorimeter. Primary crystalline iron-bearing phases were goethite and lepidocrocite, and iron phases converted to hematite upon heating. Quartz was nearly ubiquitous except for synthetic pigments. Gypsum, bassinite, calcite, and ettringite were found in active treatment sediments. Iron concentrations from highest to lowest were synthetic pigment>wetland sediment>natural pigment>active treatment (untreated sediments varied more widely), and manganese was highest in actively treated sediments. Loss on ignition was highest for passively treated sediments. No clear trends were observed between quantified color parameters (L^*, a^*, b^*, and Redness Index) and chemical compositions. Because sediments from passive treatment are similar in chemistry, mineralogy, and color to natural pigments, the mine drainage sediments may be an untapped resource for pigment.

Key words Mine drainage · Sediments · Mineralogy · Treatment

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Introduction

Iron oxides have been used as pigment for millennia. Natural and synthetic iron oxides are used in a wide range of applications including paints, stains, magnetic recordings, plastics, and building materials. Naturally-occurring oxides and hydrated oxides of Fe, Al, and Mn are concentrated by the weathering process. These natural red/yellow/brown pigments are currently mined as resources on a small scale because specific colors are the desired resource, and the weathering horizons in which the desired colors are found are much smaller than deposits of Fe mined for steel manufacture (Jones 1978). Jolly and Collins (1980) discussed the geological occurrence of natural iron oxide pigments. The properties that determine the utility of natural and synthetic pigments include chemical composition, mineralogy, color, tinting strength, oil adsorption, grain size and shape, and chemical impurities (Jones 1978).

Acid mine drainage (AMD) is a significant source of pollution and also a potential resource due to its high metal loading. The areal extent of streams affected by coal mining resulting in AMD is quite large. Herlihy and others (1990) concluded that approximately 10% of the stream reaches in the Northern Appalachian subregion were acidic in 1986 during baseflow conditions due to AMD. Cleanup costs for Pennsylvania alone are estimated at $15 billion for abandoned mines, assuming no materials can be recovered as resources. Currently, federal and state governments along with mine operators are paying to remediate and attempting to prevent AMD. Mine drainage sediments from treatment facilities are currently considered a waste material which must be disposed of. Mine drainage sediments are rich in Fe, which gives rise to the ochreous colors, and these sediments may represent a vast untapped resource if they can be recovered economically in a usable form. If not independently economical, such recovery and utilization of a resource could subsidize the remediation of mine drainage. The potential mass of ferric oxide recovery is high. Assuming the solid precipitate to be $Fe(OH)_3$, a drainage of 10^6 l day^{-1} with a concentration of 25 mg Fe l^{-1} Fe will yield 17 metric tons of $Fe(OH)_3$ year^{-1}.

Numerous Fe hydroxide solids including jarosite, goethite, ferrihydrite, and amorphous Fe hydroxides have been reported to form in subaqueous AMD systems. This paper does not consider Fe hydroxysulfates formed in subaerial environments (see, for example, Cravotta 1994) because they are not likely candidates for recovery and utilization due to low volume and acidic nature. Karlsson and others (1988) examined stream bed sediments from cores, but did not isolate mineral phases. Chapman and others (1983) found the major component of AMD sediments to be a largely amorphous hydrous iron oxide with the approximate empirical formula $Fe_{1.0}Si_{0.3}(SO_4)_{0.2}Al_{0.1}$ with trace amounts of As, K, and Pb (no water listed in formula). They suggest that the SO_4^{2-} is adsorbed to surfaces. Bigham and others (1992) suggest that some of the precipitates referred to in the literature as "amorphous ferric hydroxide" are actually composed of a poorly crystalline oxyhydroxysulfate of Fe. Recently (Bigham and others 1994), this material has been declared a mineral, schwertmannite. No studies characterize sediments from passive wetland treatment in terms of mineralogy or color; Fish and others (1996) examined the chemistry and some physical properties of such sediments.

Most studies of resource recovery have focused on active chemical treatment involving daily addition of reagents. At the turn of the century, Heckman (1908) patented a method of recovering pigments by chemically treating mine drainage. Kaplan (1930) suggested a similar method for recovery of resources from mine waters. However, the variability of the sludge composition from active treatment facilities has apparently prevented utilization of the sludge as a resource. Brown and others (1994) found up to tenfold variations in the concentrations of Fe, Mn, Al, and Ca in sludges from different active treatment methods. Osman and others (1970) also reported large variations in Fe, C, Mg, Ca, and Al. Lovell (1970) considered sludges to be of no use because of the high compositional variability. Rao and others (1994) suggested sequential recovery of metals as hydroxides by varying pH, potentially overcoming some of the problems with variability.

Within the past two decades, wetland treatment of coal mine AMD, with or without the addition of limestone, has been increasingly used because it can be more cost-effective than active treatment especially for smaller discharges. Wetland treatment also produces precipitated sediments, and the sediment composition and color varies with the influent water composition and with the treatment method. However, Fish and others (1996) suggest that sediments from passive wetland treatment facilities have Fe concentrations in ranges similar to natural and synthetic pigments, thus warranting attention as resources. Sediments from the passive treatment of coal mine drainage, particularly those from systems that are not extremely acidic, may hold the most promise for use as resources. Because pH values are often circumneutral and the source rocks do not contain the high concentrations of trace metals (Cu, Zn, Cd, Ni and others) that are commonly associated with metal ore deposits, the treatment process is simpler and the sediments produced are more uniform.

This study compared precipitated sediments from untreated mine drainage, actively and passively treated mine drainage, three natural pigments, and two synthetic pigments. The primary objective was to provide background data on the similarities and differences in the major element composition, mineralogy, and color of these Fe-rich solids. If mine drainage sediments are to be utilized as pigments, the colors and compositions must be of consistent quality. In addition, it would be advantageous to be able to predict sediment color based on simple assays. The two primary hypotheses were that (1) sediments from AMD wetland treatment would be quite similar in composition and color to pigments, and would show higher Fe concentrations and less variation in chemistry and color than sediments from active treatment, thus holding more promise as resources; and (2) the sediment colors could be predicted based solely on knowledge of the sediment chemistry. Although they may be important for resource utilization, we have not addressed issues of trace element sequestering by AMD sediments, nor did we examine aging, diagenesis or spatial variation of AMD sediments in this study.

Methods

Grab samples of sediment were collected from untreated and actively and passively treated mine drainage in central and western Pennsylvania in the anthracite and bituminous coal regions. Table 1 gives the characteristics of each sample. Five commercial pigment materials were also examined. All samples were dried at 60 °C in an oven and stored in a desiccator. Dried samples were ground with a hand mortar and pestle sufficiently to disaggregate particles. Samples for color analysis were sieved to <25 mesh (0.710 mm).

Samples for X-ray fluorescence (XRF) and fusion-inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were sieved to <80 mesh sieve (0.180 mm). Oven-dried samples were subsequently fired in a muffle furnace at 900 °C for at least 6 h to determine loss on ignition (LOI). The remnant fired material was used in XRF and fusion-ICP-AES analyses. Samples for XRF analysis were fused with lithium tetraborate $\pm Al_2O_3$ as a dilutant to form glass disks (Fe_2O_3 was determined from a 1:4 dilution with Al_2O_3; all other major elements were analyzed with no dilution) and analyzed using a Phillips 2400 X-ray fluorescence spectrometer with appropriate standards. Fusion-ICP-AES analyses were carried out at ACTLABS, Ontario, Canada. C and S were analyzed by LECO induction furnace.

Oven-dried samples were mixed in an acetone slurry and mounted on a low-background quartz plate for powder X-ray diffraction (XRD) using a Phillips XRG-3000 X-ray diffractometer operated at 40 kV and 30 mA from 4° to 80° 2Θ. Minerals were identified based on visual comparison of patterns to standard Joint Committee on Powder Diffraction Standards data (International Centre for Diffraction Data 1993). Colors of oven-dried powders (<25 mesh) were quantified using a Minolta CR-300 tristimulus colorimeter. The colorimeter returns quantitative values for both Munsell renotation (chroma, hue, value) and

Table 1
Nature of samples and minerals identified by X-ray diffraction (*XRD*). Divisions in this table are for untreated, passive treatment, active treatment, natural pigment, and synthetic pigment. The pH given is for water in the treatment facility nearest the sample site (*goe* goethite, *qtz* quartz, *lep* lepidocrocite, *kaol* kaolinite, *ill* illite, *cc* calcite, *bass* bassanite, *clay* unidentified phyllosilicate, *gibb* gibbsite)

Label	Sample number	Treatment method	pH	Minerals by XRD
untr	10	Untreated deep mine	6.1	goe
untr	23	untreated deep mine	3.5	goe, qtz
untr	24	untreated surface mine	3.5	goe, qtz
untr	25–29	untreated deep mine	3.5–6	goe ± qtz
untr	30–32	untreated surface mine	4.5	goe, qtz
SV	1	deep mine, alkaline	6.3	goe, qtz
CG	4	deep mine, alkaline	6.1	goe, qtz ± lep
TN	7–9	surface mine, alkaline	6.2	goe, qtz ± lep, kaol, ill
HB	11–13, 34, 35, 38, 40, 42	aband, well, alkaline	3.5–6	geo ± qtz, lep, kaol, cc
MO	16	surface mine, alkaline	6.3	goe, qtz, lep
FIL	37	surface mine, alkaline	6.2	goe ± qtz
BRA	33	lime slurry	11	gyp, cc, bass, goe
BRA	36	lime slurry	11	gyp, cc, bass, goe, qtz
BRA	48	fly ash or NH_3	3	goe, qtz, ettringite
RC	43	lime slurry, holding pond	7	qtz, kaol, clay
RC	45	lime slurry, holding pond	7	goe, qtz
RC	47	lime slurry, clarifier	7	qtz, goe
HOO	19	Hoover 52 raw sienna	na	goe, qtz, rutile?
HOO	20	Hoover 33 ochre	na	goe, qtz, rutile?
HOO	21	Hoover natural yellow	na	goe, qtz, gibb, kaol
BF	14	Bayer red 130M	na	hematite
BF	15	Bayer yellow 940	na	goe

the 1976 CIE (Commission Internationale d'Eclairage) $L^*a^*b^*$ notation, which are interconvertable. L^* is a measure of "lightness" (an L^* value of 100 is pure white), a^* is red, and b^* is yellow. Redness Index (RI; see Tarutis and Unz 1994) in this report is calculated as log $[C/(H^*V)]$ where C and V are Munsell chroma and value, respectively, and H^* is a modified Munsell hue ($H^* = 5.0$ for 5.0R, 15 for 5YR, 25 for 5Y).

Results and discussion

X-ray diffraction

The minerals identified by XRD are shown in Table 1 for groups of samples (rather than for individual samples). Table 2 gives a list of mineral names and chemical formulae for minerals discussed in the text. Variously crystalline goethite was nearly ubiquitous in AMD sediments and natural pigment, and detrital quartz was also common. Several AMD sediments from passive treatment also contained lepidocrocite and trace quantities of calcite, kaolinite, and illite. The mineralogy from active treatment varied widely, and for two samples, crystalline Fe hydroxides (goethite) were only found in trace quantities, whereas calcite, gypsum, and bassinite were predominant. The synthetic red and yellow pigments were composed of hematite and goethite, respectively.

The conversion from X-ray amorphous and variously crystalline Fe hydroxides to well-crystallized hematite is typical of the behavior of most AMD samples and natural pigments upon heating. Figure 1 is an X-ray diffractogram of sediment from untreated mine drainage (10) before and after LOI, and of a commercial synthetic pigment product (14). This red synthetic pigment was heated during manufacture and is mainly composed of well-crystallized hematite. Before LOI, the mine drainage sample contains goethite; after LOI, this sample is predominantly hematite, apparently with a trace amount of an SiO_2 phase (cristobalite and a synthetic phase both match this low-intensity peak at 21.7° 2Q). Figure 2 compares diffractograms for sediment from an anoxic limestone drain/passive wetland treatment (42) to a natural commercial pigment product (19; raw sienna) from a soil horizon, both before and after LOI. Both samples contain fairly well-crystallized goethite; the pigment also contains quartz and probably rutile (0.5 wt % TiO_2). Upon heating, both samples converted to well-crystallized hematite. Fewer different mineral phases are present in sediments from passive wetland treatment systems than sediments from active chemical treatment. Figure 3 shows the mineralogy of sediments from two passive systems. Both sites contain goethite of varying crystallinity, and some of the samples contain detrital quartz. Sample 38 contains lepidocrocite, and sample 34 contains a trace of kaolinite and possibly a detrital feldspar.

Figure 4 shows the mineralogy of two sediments from active treatment facilities. Sample 47 (Rausch Creek Mine Drainage Treatment Facility, Valley View, PA) is primari-

Table 2
Chemical formulae of minerals discussed in text

Potential resource minerals		Detrital/secondary minerals	
Mineral name	Formula	Mineral name	Formula
goethite	αFeOOH	illite	$KAl_2(Si_3Al)O_{10}(OH)_2$
hematite	Fe_2O_3	kaolinite	$Al_2Si_2O_5(OH)_4$
lepidocrocite	γFeOOH	quartz	SiO_2
		rutile	TiO_2
		gibbsite	$Al(OH)_3$
Mine drainage minerals not found in this study		**Minerals formed due to limestone/lime addition**	
ferrihydrite	$Fe_5O_7(OH) \cdot 4H_2O$	bassanite	$CaSO_4 \cdot 0.5H_2O$
jarosite	$(Na,K)Fe_3(OH)_6(SO_4)_2$	calcite	$CaCO_3$
schwertmannite	$Fe_{16}O_{16}(OH)_{9.6}(SO_4)_{3.2} \cdot 10H_2O$	ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
		gypsum	$CaSO_4 \cdot 2H_2O$

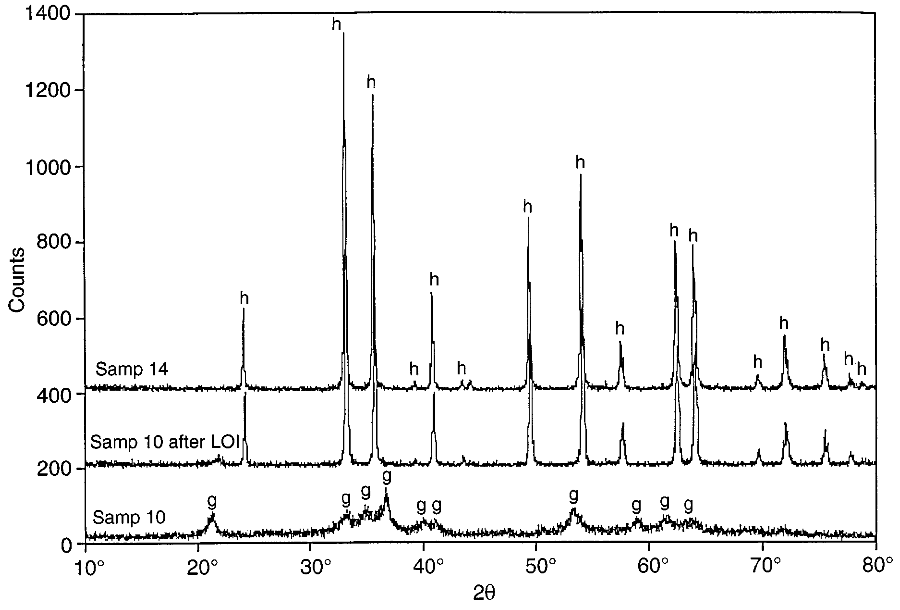

Fig. 1
X-ray diffractogram of untreated acid mine drainage sediment (sample 10) before and after loss on ignition compared to synthetic red pigment (sample 14)

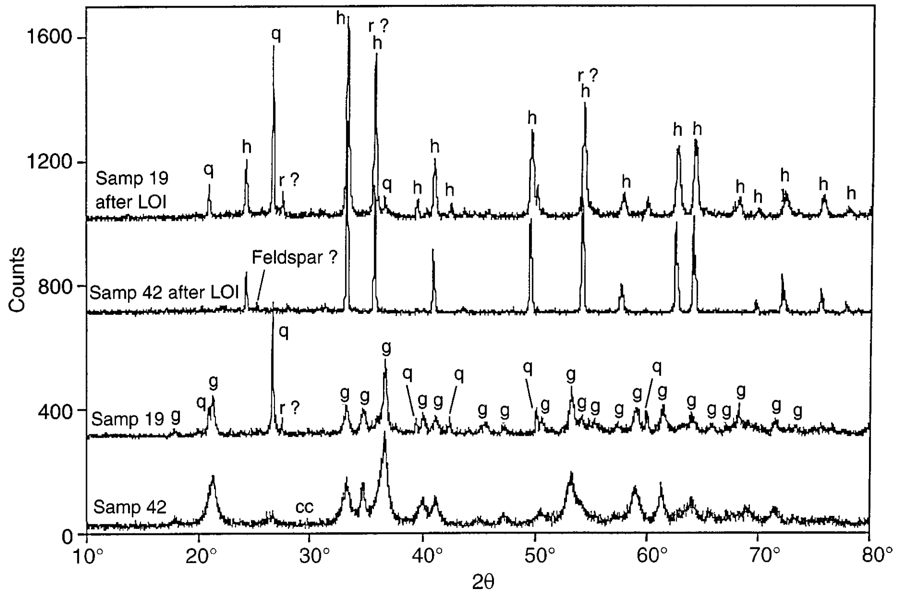

Fig. 2
X-ray diffractogram comparing sediment from passive treatment (sample 42) and natural raw sienna pigment (sample 19) before and after loss on ignition (LOI)

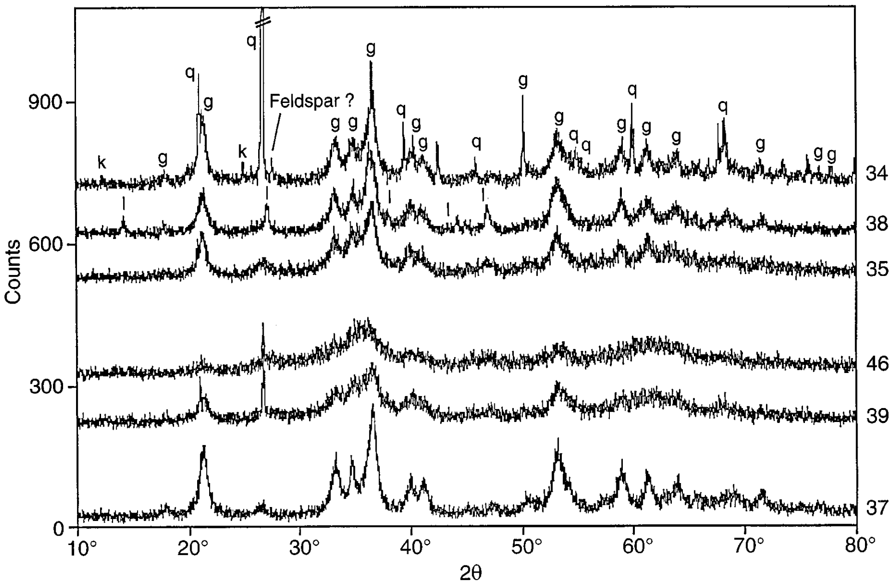

Fig. 3
X-ray diffractogram comparing sediments from Filson (samples 37, 39, 46) and Howe Bridge (samples 34, 35, 38) passive treatment facilities. Prominent peaks not labeled are due to goethite

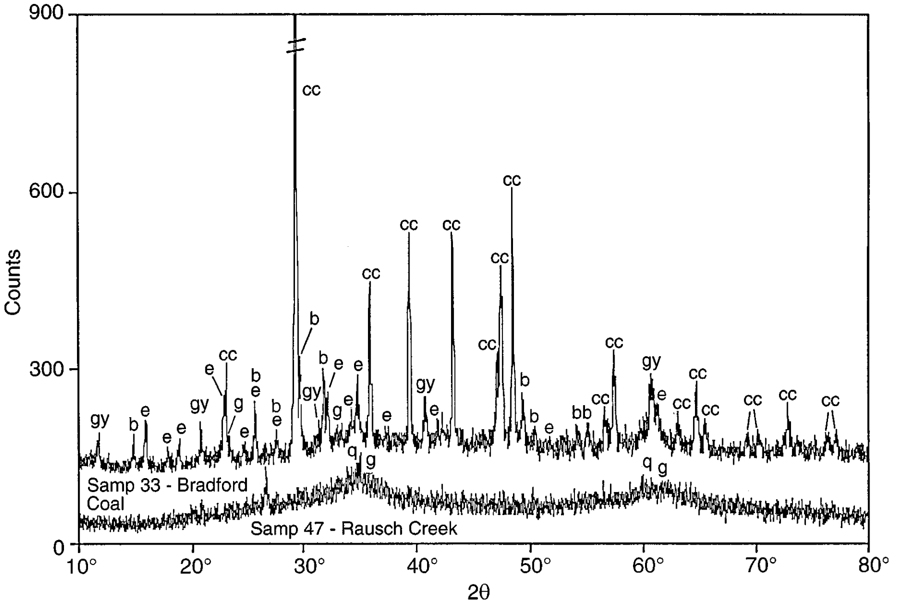

Fig. 4
X-ray diffractogram comparing sediments from two active treatment facilities. Minerals identified include: *cc* calcite, *g* goethite, *gy* gypsum, *b* bassinite, *e* ettringite, *q* quartz

ly composed of poorly crystallized goethite with a trace of detrital quartz. The low intensities suggest that very little crystalline material is present. A sample from a holding pond at this facility (43, not shown in Fig. 4) also contained poorly crystallized goethite along with quartz, kaolinite, an unidentified hydrous phyllosilicate (clay) and lepidocrocite. A core of this holding pond also showed significant color variations with depth, suggesting that the composition and mineralogy vary with time. The only crystalline Fe hydroxide in sample 33 (from ponds in which a lime slurry raised pH as high as 11) was a trace of goethite. In this sample calcite, gypsum, bassinite, and ettringite (commonly formed in cement) precipitated due to the addition of lime.

Bigham and others (1992) correlated the distribution of mine drainage minerals to effluent pH. They found jarosite between pH 2.5 and 3.5, schwertmannite (referred to as “mine drainage mineral” before acceptance of the name schwertmannite) between pH 2.8 and 6.3, goethite between pH 2.5 and 7.3, and ferrihydrite between pH 5 and 8. In this study, samples from treated mine drainage sediment contained no jarosite, ferrihydrite, or schwertmannite (although overlapping of quartz and goethite peaks may have hidden trace quantities of schwertmannite). Goethite and lepidocrocite were the only Fe-bearing minerals observed in sediments from passive treatment facilities. It was assumed, but not documented, that X-ray amorphous Fe hydroxides were also present. The passive treatment facilities exhibited more consistent mineralogy and higher concentrations of Fe-rich minerals (as documented by X-ray intensities) than active treatment facilities.

Chemical composition

Table 3 presents LOI and oxide or elemental compositions (wt % by fusion-ICP-AES) for all mine drainage sediments and pigments in this study. XRF and fusion-ICP analyses gave similar results with the following exceptions. Na_2O was significantly lower from fusion-ICP (for example, 0.1% by ICP compared to 0.8% by XRF). TiO_2 was consistently approximately 5% lower from fusion-ICP. MgO showed up to 300% variation for samples under approximately 0.1 wt %, but less than 10% variation was noted for samples over 0.1 wt %. Figure 5 shows the average and range of concentrations for selected ele-

Table 3

Loss on ignition (*LOI*), oxide or elemental compositions, and color parameters (*na* data not available). Divisions in this table are for untreated, passive treatment, active treatment, natural pigment, and synthetic pigment. Ranges for other oxides include K_2O from <0.01 to 2.85, Na_2O from <0.01 to 1.08, P_2O_5 from 0.01 to 1.03 (except sample 42 = 4.51)

	Sample	LOI	CaO	MgO	TiO_2	Al_2O_3	SiO_2	Fe_2O_3	MnO	C	S	Color parameters		
		%	%	%	%	%	%	%	%	%	%	*L**	*a**	*b**
untr	10	17.77	0.66	0.05	<0.01	0.12	5.11	72.3	0.04	0.28	0.50	52.99	18.19	45.42
untr	23	30.54	<0.01	0.02	0.14	1.61	10.3	53.2	<0.01	0.09	3.19	45.17	17.34	44.99
untr	24	33.41	0.02	0.04	0.12	1.19	6.95	55.0	<0.01	0.57	3.67	36.78	16.71	36.11
untr	25	30.50	0.13	0.16	0.24	4.80	14.5	46.9	0.04	11.1	1.21	47.54	15.73	37.50
untr	26	32.58	0.16	0.05	0.02	7.82	2.95	53.0	<0.01	2.17	1.66	53.15	18.64	42.30
untr	27	28.42	0.05	<0.01	0.01	2.36	2.21	61.4	<0.01	0.13	1.99	51.78	22.82	49.03
untr	28	30.99	0.20	0.04	0.03	10.3	5.54	49.6	<0.01	0.96	1.42	56.61	18.44	45.33
untr	29	34.91	<0.01	0.01	<0.01	0.53	0.56	59.3	<0.01	0.46	5.34	42.00	17.68	44.75
untr	30	32.87	<0.01	0.04	0.13	4.12	9.72	50.0	0.04	4.68	2.54	46.49	16.02	39.25
untr	31	50.52	<0.01	0.03	0.07	20.3	7.11	20.1	0.11	na	na	50.37	8.28	28.73
untr	32	39.90	0.10	0.09	0.14	11.2	13.0	31.6	1.52	11	0.8	51.45	11.86	36.07
SV	1	35.12	0.55	0.07	0.04	0.64	5.35	54.6	0.04	1.02	0.60	37.62	21.41	37.50
SV	2	19.41	0.93	0.28	0.23	3.48	16.5	55.1	0.22	2.65	0.52	44.13	20.30	39.85
SV	3	18.38	0.85	0.17	0.10	1.73	9.28	65.3	0.07	1.73	0.54	41.91	21.15	39.8
CG	4	18.05	0.80	0.06	0.02	0.38	7.93	67.6	0.02	0.43	0.52	47.43	23.21	46.94
CG	5	18.05	0.78	0.07	<0.01	0.35	7.94	68.0	0.01	0.18	0.53	47.99	23.48	47.99
CG	6	17.81	0.90	0.08	0.01	0.38	7.22	69.1	0.03	0.70	0.52	49.56	21.26	44.24
TN	7	15.98	0.60	0.28	0.27	3.59	23.8	51.7	0.35	0.51	0.65	42.54	21.56	40.81
TN	8	14.67	1.22	0.11	0.05	0.56	6.87	70.8	0.37	2.49	0.29	46.12	14.12	38.16
TN	9	12.42	1.17	0.10	0.08	0.57	7.94	71.9	0.66	0.29	0.36	25.84	18.30	24.82
HB	11	16.87	0.14	0.07	0.05	0.61	5.13	72.3	0.21	0.44	0.66	54.43	17.53	54.26
HB	12	16.17	0.16	0.09	0.11	1.01	11.2	67.1	0.20	0.44	0.84	51.03	15.13	47.12
HB	13	17.23	0.13	0.03	<0.01	0.15	1.99	73.5	0.24	0.47	0.69	54.29	13.87	47.17
HB	34	20.69	0.05	0.12	0.31	2.88	23.1	34.9	0.02	1.7	2.16	48.49	10.99	41.42
HB	35	29.38	na	na	na	na	na	na	na	na	na	54.63	19.47	53.67
HB	38	22.41	0.18	0.07	<0.01	0.12	1.63	69.1	0.14	0.15	1.26	50.42	20.45	52.15
HB	40	21.28	0.08	0.04	0.03	0.34	2.32	69.7	0.10	0.67	1.29	52.6	11.66	51.32
HB	42	14.75	1.59	0.11	<0.01	0.07	1.92	71.6	0.33	0.4	0.59	51.9	11.96	47.35
HB	44	23.81	0.13	0.08	0.01	0.18	1.11	68.4	0.06	0.36	2.85	50.96	15.5	53.52
MO	16	17.73	0.14	0.10	0.11	2.02	7.73	66.1	0.36	0.66	0.81	49.18	19.13	45.84
MO	17	17.51	0.19	0.07	0.06	1.02	4.89	69.0	0.41	0.5	0.58	48.89	18.25	46.72
MO	18	17.60	0.20	0.06	0.06	0.90	4.02	71.1	0.42	0.38	0.44	46.52	17.18	44.72
FIL	37	25.63	0.37	0.02	<0.01	0.14	1.82	54.5	0.39	0.43	0.3	47.85	15.94	46.43
FIL	39	21.28	1.08	0.09	0.10	1.27	8.24	61.5	1.37	0.41	0.19	38.94	17.09	35.74
FIL	41	50.05	0.09	0.04	0.02	0.22	1.98	43.9	0.17	1.1	0.3	46.13	17.45	40.86
FIL	46	27.66	1.78	0.09	0.02	0.35	2.57	60.6	0.47	0.39	0.36	47.67	23.21	48.23
BRA	33	37.45	29.0	5.80	0.01	2.39	1.81	9.55	0.21	5.2	4.99	59.68	7.64	27.15
BRA	36	39.00	38.5	5.05	<0.01	2.58	1.77	7.09	0.30	7.54	3.11	62.1	10.13	33.38
BRA	48	24.38	0.02	0.24	0.21	4.69	12.1	54.3	0.10	1.21	2.34	61.83	10.76	53.16
RC	43	34.66	2.44	3.57	0.29	8.98	20.7	22.4	3.96	13.7	0.45	25.17	1.72	11.06
RC	45	32.39	3.35	4.17	0.09	5.78	14.8	31.2	4.95	3.21	0.44	25.11	4.11	14.07
RC	47	31.25	2.77	4.20	0.11	6.25	15.5	31.5	5.36	2.81	0.57	24.37	3.79	13.94
HOO	19	8.96	0.07	0.88	0.53	9.96	31.8	41.1	0.74	<0.06	0.07	59.64	9.26	41.70
HOO	20	9.15	0.10	0.76	0.52	9.21	31.8	42.9	0.55	0.15	0.06	60.89	8.69	38.18
HOO	21	13.72	0.22	0.09	0.24	9.79	5.44	66.7	0.06	0.08	0.05	61.64	10.77	46.66
BF	14	0.37	0.02	<0.01	0.02	0.07	2.84	89.3	0.08	0.18	0.05	38.98	31.80	24.75
BF	15	13.30	<0.01	<0.01	0.05	0.05	<0.01	78.5	0.02	<0.06	0.69	64.05	13.74	62.66

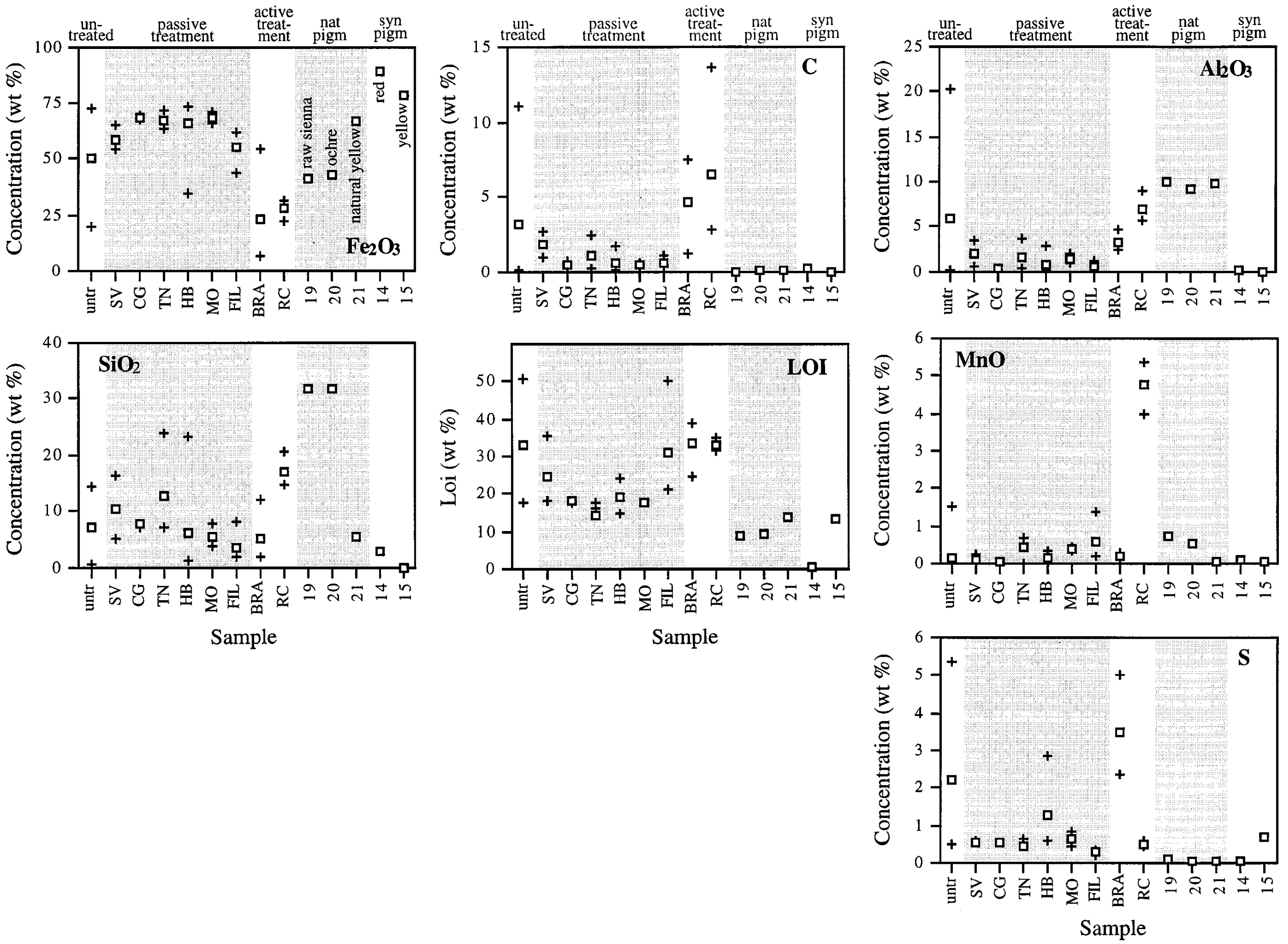

Fig. 5
Minimum and maximum (+) and average () weight percents of selected oxides, elements, and loss on ignition (*LOI*) for all samples. Pigment values are individual samples rather than averages

ments, oxides, and LOI. Similar samples (untreated, passive, active, natural and synthetic pigment) are grouped together, and paragraphs immediately below refer to Fig. 5.

Fe is primarily responsible for the red and yellow colors in soils and mine drainage sediments. The Fe_2O_3 concentration in passive treatment sediments exhibits relatively little variation and is generally as high as or higher than in the natural pigments; this behavior was also noted by Fish and others (1996). Both passive treatment sediments and natural pigments had lower Fe_2O_3 concentration than synthetic pigments. This study did not examine the spatial distribution of elements within facilities, but Tarutis and Unz (1994) documented decreasing Fe concentrations and decreasing redness of sediments with distance along a flowpath in one wetland treatment facility. The Fe_2O_3 concentrations in most samples from active treatment facilities are diluted by Ca, Mg, Si, Al, S, and C and are noticeably lower than in other samples.

Because hydrated Al oxides are often white, increasing Al concentrations would tend to dilute red and yellow colors of sediments. The Al_2O_3 concentrations for most AMD samples were <5%, with active treatment facilities having slightly higher Al_2O_3. The natural pigments had approximately 10% Al_2O_3 bound in gibbsite or kaolinite. However, no Al-bearing phases were observed using XRD for sample 19. The synthetic pigments had <0.1% Al_2O_3. Most passive wetland treatment facilities will likely be low in Al because, until very recently, these facilities have been located where the influent water is low in Al to avoid the clogging of anoxic limestone drains by Al hydroxides (Skousen 1991). Kepler and McCleary (1997) recently presented a method to treat Al in passive systems, so wetland systems may have higher Al concentrations if this technology is used in the future.

The SiO_2 concentrations show relatively wide variations both within and among sample types. All of the AMD samples have lower SiO_2 than two of the natural pigments, and the synthetic pigments have <3% SiO_2. The SiO_2 in the AMD samples is primarily bound in detrital quartz, with traces of hydrous phyllosilicates.

Mn oxides are gray to black and can cause darker coloration of sediments, diluting reds and yellows from Fe oxides. All samples had MnO concentrations less than 2%

except for samples from the Rausch Creek active treatment facility. Mn is difficult to remove in passive wetland treatment (Hedin and others 1994) but is effectively removed by active treatment.

C concentrations are highest in the active treatment sediments, due to the presence of calcite in the Bradford Coal samples and the presence of fine detrital coal and stream organic matter in the Rausch Creek samples. C in the passive treatment samples (<3%) is presumably from bacteria (see Robbins and Norden 1994) and detrital organic matter, although three Howe Bridge samples had traces of calcite present. The pigments all had <0.2% C.

S concentrations were <1% for most of the passive treatment samples and for all of the pigment samples. S concentrations were higher in the untreated AMD sediments than in those from passive treatment; high S concentration may indicate adsorption or precipitation of Fe hydroxysulfates in lower pH environments. S was highest in the actively treated Bradford Coal samples, which contained gypsum.

LOI is consistently higher in the AMD samples than in the pigment samples. Most AMD samples had 15–35% LOI, although two outliers (31 and 41) had 50% LOI. For comparison, dehydration of pure $Fe(OH)_3$ to make Fe_2O_3 would result in a 25.3% LOI, and dehydration of pure FeOOH would result in a 10.1% LOI. C and S would be volatilized during heating for LOI.

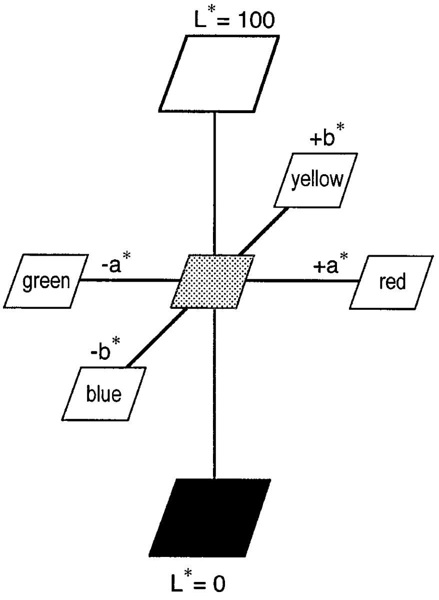

Fig. 6
Schematic representation of 1976 Comission Internationale d'Eclairage (CIE) *L*a*b** color space (after Torrent and Barron 1993)

Color variations

*L*a*b** color values for all samples are shown in Table 3. The 1976 CIE *L*a*b** color space (see Fig. 6; after Torrent and Barron 1993) provides a quantitative method to compare color variations between sediment and pigment samples. Figure 7 shows the average and range of color parameter values for groups of like samples. *L** is high for the three natural pigments (19–21) and the synthetic yellow pigment (15), which are primarily composed of goethite. The Bradford Coal samples (33, 36, 48) also have high *L** values, probably due to the presence of calcite, gypsum, and ettringite, which have a white streak (the color of the powdered mineral). Sample 48 also contains goethite. The Rausch Creek active treatment samples were notably darker than all others samples and had the lowest *L** values. *L** values for the passive treatment

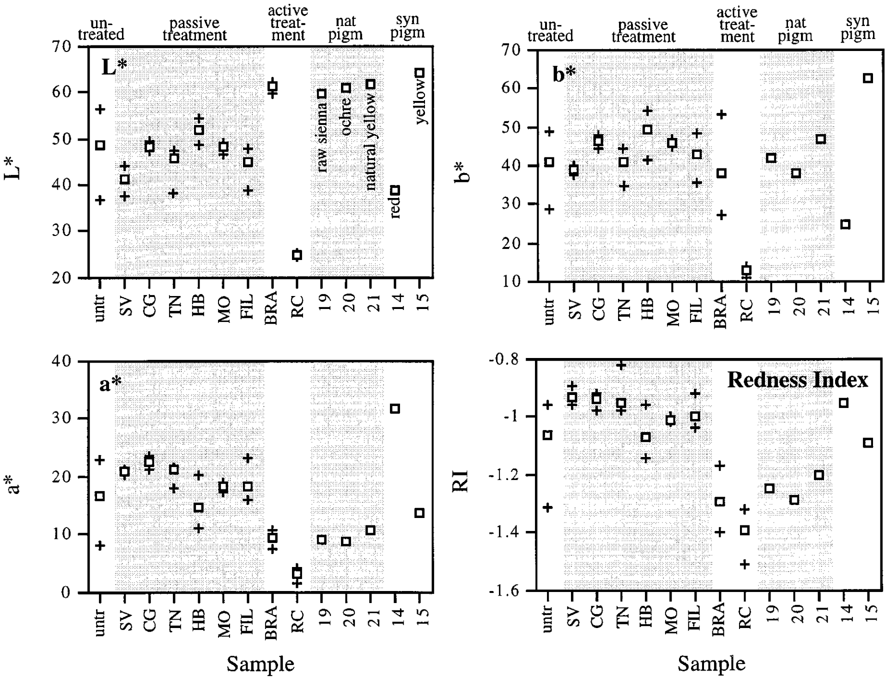

Fig. 7
Minimum and maximum (+) and average color parameters for all samples. Pigment values are individual samples rather than averages

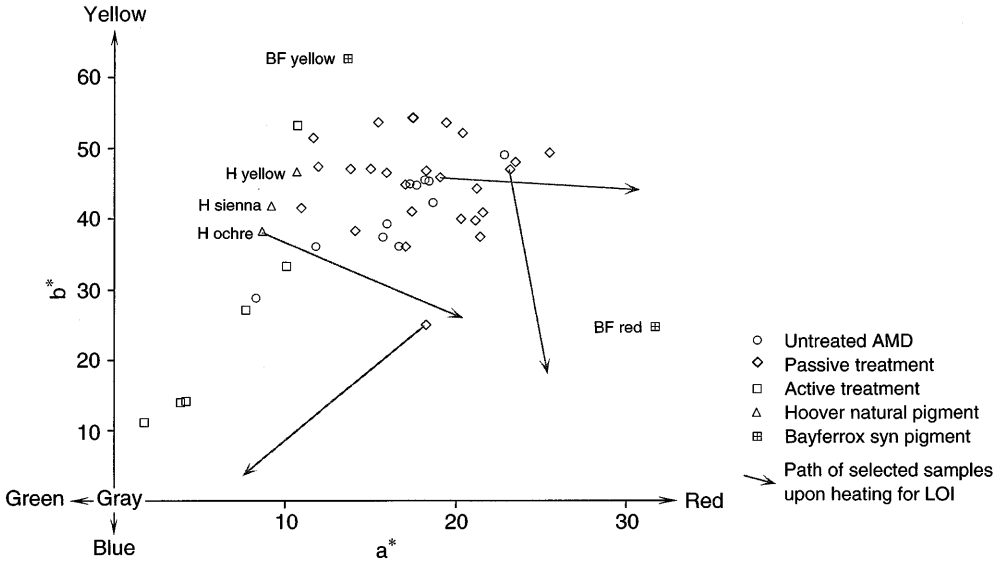

Fig. 8
Mine drainage sediments and pigment samples projected onto the a^*-b^* plane of $L^*a^*b^*$ color space

samples were lower than for most of the pigments, with $38 < L^* < 54$.

The a^* values for passive treatment sediment were consistently higher than those for active treatment and natural pigment samples, indicating that the passive treatment sediments had a greater red component. The synthetic red pigment (14) had the highest a^* value. Passive treatment sediment b^* values were similar to the natural pigment b^* values, although the passive treatment sediments exhibited a slightly more variation. The synthetic yellow pigment (15) had the highest b^* value.

Torrent and Schwertmann (1987) used a projection onto the a^*b^* plane of the CIE $L^*a^*b^*$ color space to compare mixtures of synthetic hematite and kaolinite to hematite-rich red bed rocks. In Fig. 8, this space is used to compare AMD sediments to Fe oxide pigments. The three natural pigments (19–21) fall quite close to some of the AMD sediments from both passive treatment and untreated systems. The three samples in the lower left corner of Fig. 8 are from the Rausch Creek active treatment facility and are much browner than any other sample. The synthetic red pigment (14) is much redder than any of the other samples because this synthetic sample is almost entirely composed of hematite. Heat treatment might allow for the use of AMD sediments (yellow-orange before heating) as red pigment, although quality control of the color would not be as consistent as for synthetically produced pigments. To test this hypothesis, 17 samples were analyzed for color following LOI. If sediments become redder upon heating, the trajectory in a^*b^* space should trend toward a^* and away from b^*. Upon heating, all samples experienced changes in a^* and b^*, and the color changes of four samples are shown in Fig. 8 as examples. Only six of the 17 samples clearly moved away from b^* toward a^*. Seven samples showed decreasing b^* with little change in a^*, and four samples showed decreasing a^* values. Therefore, no general rule for color changes trends can be established, and the color change upon heating for a particular sample must be determined empirically.

Redness Index

Calculation of the RI provides another method to compare color variation of sediment and pigment. Figure 7 shows that the RI was consistently high for passive AMD sediments and for the synthetic red pigment (14). Most of the active treatment sediments had slightly lower RI than the natural pigments.

Figure 9 shows RI versus Fe_2O_3 concentrations. Data from this study do not fit a linear trend well; r^2 for all samples in this study is 0.52. Removal of data from active treatment facilities worsens the fit, giving an r^2 of 0.30. Samples from passive treatment show no correlation at all (r^2 of 0). Tarutis and Unz (1994) found that sediments from a constructed wetland for mine drainage treatment and hematite-bentonite standard mixtures give linear fits with r^2 values of 0.72 and 0.99, respectively. The data for Hurst's (1977) hematite-quartz mixtures plot above the Tarutis and Unz data, and data for Hurst's goethite-quartz mixtures plot below the Tarutis and Unz data. Hurst (1977) suggests that dilution of the red pigment agent is not the only factor that affects color, and that using white clay as a dilutant would yield data falling closer to a straight line, as is the case for the Tarutis and Unz (1994) data for their hematite-bentonite standard mixtures. The RI for the highest concentration standard ($RI = -0.4$, $\log Fe_2O_3 = 5.96$) from the Tarutis and Unz (1994) data is much higher than the RI for sample 14 from this study ($RI = -0.95$, $\log Fe_2O_3 = 5.95$). This behavior might be explained by the association of hematite into crystal clusters whose size and density influence optical properties (Torrent and Schwertmann 1987). Other factors which may contribute to the lack of obvious correlation of RI to Fe concentration include particle size and the optical properties of the dilutants in both standards (quartz, bentonite) and samples (organic matter, sil-

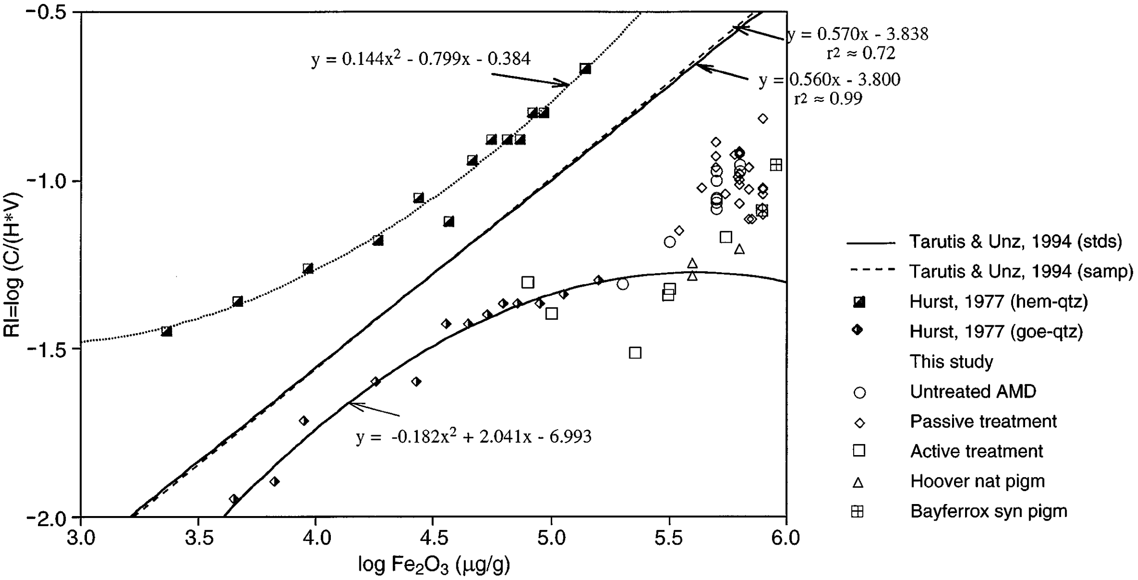

Fig. 9
Comparison of relationships between redness index and Fe_2O_3 concentrations. *Curves* are drawn through Hurst (1977) data for goethite-quartz and hematite-quartz mixtures. A least-squares fit only is shown for Tarutis and Unz (1994) data (Fe converted to Fe_2O_3)

icate clay minerals, Al hydroxides, detrital minerals, and minerals resulting from excess addition of base such as calcite and gypsum). Moisture effects on color (Shields and others 1968) should be minimal because all samples were dried. The mineralogy of natural sediments may be so complex that use of RI versus Fe_2O_3 concentrations may not have significant predictive power.

Relationship between sediment chemistry and color-regression analyses

One original hypothesis of this work was that the color of sediments associated with mine drainage, as defined by L^*, a^*, and b^*, could be statistically correlated to the chemical composition of the samples. If color were a function of chemical composition alone, such a correlation would provide a simple method to evaluate the color of a sediment. However, other variables include mineralogy, particle size, moisture content, organic matter, and the nature of the dilutant (non-Fe-bearing minerals). This study investigated these complex natural systems in search of relationships which might prove useful in predicting the colors of AMD sediments; analyzing chemical composition is a necessary first step. The determination of other variables listed above significantly increases the complexity of the analytical scheme. For example, if data on the concentration of Fe phases (for example, goethite, amorphous Fe hydroxides, lepidocrocite) are required instead of chemical compositions alone in order to predict color, this approach would require more extensive research to quantify the concentration of each mineral and amorphous phase.

To begin the search for correlations, scatterplots of L^*, a^*, and b^* versus oxide and element concentrations (Table 3) were visually examined. In addition, an artificial variable called “white minerals” was created by summing K_2O, CaO, Na_2O, MgO, TiO_2, Al_2O_3, and SiO_2 percentages. Hurst (1977) discusses the masking of Fe coloration by solid phases whose true color (streak) is white; in soils these minerals include kaolinite, gibbsite, boehmite and quartz or amorphous Si. The rationale for the variable white minerals is that the above oxides are likely to be bound in solid phases that are predominantly white when grain size is small; thus these elements might contribute to L^*. Fitting the data using univariate least squares regressions for all treated and untreated mine drainage sediments gave surprisingly weak correlations between color values and composition values. For example, the correlation coefficient, r, for b^* and Fe_2O_3 was only 0.65. MnO showed some negative correlation with all three color parameters. Multivariate linear regressions for all oxides and white minerals against L^*, a^*, and b^* were similarly unproductive. Even when ten oxides were employed as independent variables, the color variables are not “predicted” well by chemical composition alone. Although it was expected that the concentrations of Fe_2O_3, MnO, and white minerals might predict the colors of the sediments, the chemical compositions alone have little or no predictive power for color parameters.

It appears necessary to include some other variables than simply chemical composition in order to reliably predict color. One possible approach would be to use the Kubelka-Munk theory, which Barron and Torrent (1986) employed to predict the color of synthetic mixtures of hematite, goethite and deferrated soil with white standards. This approach requires use of a spectral reflectance spectrophotometer rather than a colorimeter. Another approach would be to include the concentrations of mineral phases in the statistical analyses, which significantly increases the difficulty of the analytical scheme. Because spectral reflectance spectrophotometers are not widely available, and quantitative XRD analysis is not a common industrial practice, these methods are not likely to be employed for characterization of AMD sediments for utilization on a commercial scale. This research suggests that it may be more expedient to analyze the colors of sediments individually rather than to rely on a statistical correlation employing chemistry and mineralogy to predict color.

Potential for utilization

Although prediction of colors based on chemistry alone may not be possible, the sediments from passive treatment wetlands can nevertheless be considered resources for pigment or other uses of ferric oxides. The wetland facilities concentrate Fe in a fashion similar to the way nature concentrates Fe from weathered rock. As Fish and others (1996) and this study found, sediments from wetland mine drainage treatment facilities have Fe concentrations in the range of natural pigment, and moisture contents are higher in the wetland sediments. Active treatment facilities have lower Fe concentrations (Table 3, Fig. 5) because they are diluted by the chemicals added, and the colors exhibit considerable temporal and spatial variations (based on observations of cores from a holding pond at the Rausch Creek Treatment facility not discussed in this report). Thus, sediments from active treatment show much less promise as resources. The RI, *a**, and *b** values of some sediments from passive wetland treatment also fall in the same range as natural pigments. Because of the similarities to natural and synthetic pigments, sediments from passive AMD treatment are good candidates for utilization as an Fe oxide resource.

Several factors require further investigation before utilization proves practical. After grinding to disaggregate agglomerated grains, the particle size of AMD sediments from passive treatment (Hedin Environmental 1995) is probably well within the range of natural pigment materials (up to 100 μm, <25 μm preferred; Jones 1978). The moisture content of the sediments will likely need to be lowered during processing. Variations of elemental concentration along the flowpath (see Tarutis and Unz 1994) and with depth (due to aging and changes in redox conditions) are not well known, and will be critical in quality control of any product. Faulkner and Richardson (1990) examined Fe and Mn distribution with depth in a constructed wetland using sequential extraction. Wieder and Lang (1986) also used sequential extraction, examining Fe, Mn, Al, and S distributions in an AMD peat wetlands. We are not aware of studies which examine the stability of Fe oxides from constructed wetlands. The engineering of sediment collection – whether the sediment can be economically pumped or dredged and then processed into a usable material – has yet to be addressed. Hedin (1997) has applied for a patent on a process which addresses some of these engineering and economic concerns. The stability of sediments and mobility of potentially toxic trace metals is also an open question. Fish and others (1996) provide some concentration data on trace elements associated with sediments from wetland treatment sediments, but they do not address element mobility. Specific pigment industry tests (see Fish and others 1996) will need to be carried out once some of the questions above are answered. Treatment facilities may need to be designed with collection, rather than disposal, of sediments in mind in order to prevent contamination by detrital organic matter or undesirable sediment accumulation.

Utilization of these materials could result in lowered environmental impact for two reasons. Recovery and utilization of a material that is currently an environmental contaminant could subsidize the remediation of mine drainage, especially on abandoned mine lands. Secondly, Fe oxides could be recovered from treatments facilities, thus avoiding environmental disturbances associated with the mining of Fe oxides from soil horizons. The Fe-rich sediments from passive treatment of coal mine drainage hold considerable promise as a recoverable resource for use as a pigment as well as for other uses of Fe oxides.

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