Pigment Recovered from Iron Rich Mine Water for use in Colored Concrete

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***Abstract*— Acid mine water contains high concentrations of Fe^{3+} which can be recovered as $Fe(OH)_3$, and processed to pigments.**

The aim of this study was to compare the performance of pigments, recovered from treatment of iron rich mine water, for their suitability in producing colored concrete, with that of commercially available pigments on the South African market. It was found that: (i) more colour was produced with an increase in pigment concentration, (ii) increased compressive strength with an increase in pigment concentration, (iii) reduction in slump and spread with an increase in pigment concentration (iv). Mine water pigment performed similarly to commercial pigment in the case of concrete compressive strength and spread but poorer in the case of slump.

***Keywords*— Acid mine water, colored concrete, concrete strength, iron oxide pigment**

I. Introduction

Solid and liquid waste from industrial activities, such as a result of Acid Mine Drainage (AMD) and coal fired power station operations are a great challenge. Many researchers have carried out work on solid and liquid wastes with the aim of recovering useable products.

Acid mine water contains high concentrations of metals, such as Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Co^{2+} and Ni^{2+}, which need to be removed, before the water can be further treated for desalination. The sludge produced during neutralization contains high concentrations of Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Co^{2+} and Ni^{2+}, which are categorized as toxic waste. Consequently, saleable clean water and pigment are recovered from iron rich acid mine water [1].

Pigments are defined as substances which have staining properties. Pigments are dispersed in a suitable medium, such as cement, to work as a binder. Titanium dioxide pigment emits white colour, iron oxide pigment emits red colour and magnetite emits black colour [2]. Pigments appear in a fine power, with a particles size of less than 1 µm. Pigment colors are dependent on their nature, mineralogical and chemical compositions, process of manufacturing, level of purity, forms of particles, distribution sizes and specific surface area [1]. Pigments have unique properties. Ceramic pigments have high thermal and chemical stability, $CaWO_4$ pigment has luminescent properties and Fe_3O_4 pigment has magnetic properties [2]. **Table 1** shows the most commonly used colored pigments which are based on metal oxides or mixed metal oxide.

TABLE 1: METAL OXIDES OR MIXED METAL OXIDES MOST COMMONLY USED

Color of pigments	Chemical formula of metal oxides
White	TiO_2
Black	Fe_3O_4
Red	Fe_2O_3
Yellow	FeOOH
Brown	$Fe_3O_4 + Fe_2O_3$
Green	Cr_2O_3
Blue	$CoO.Al_2O_3$

Colored and uncolored concrete is predominantly manufactured in building materials and construction industries as an important material for production of precast products such as brick and blocks, slabs and floors. Colored concrete is manufactured using pigments that have different colors, such as black, red, tan and sandstone. Color in concrete can be obtained in two ways: (i) through painting the hardened concrete surface and (ii) through addition of pigment to the concrete mix [1].

In South Africa, there is no specific manufacturer of pigments. Most pigments are imported, resulting in high prices.

The pigments used in Portland cement needs to have the following characteristics: (i) ability for coloring (that is to transfer the color to another medium according to a fixed dosage; (ii) they must be chemically non-reactive; (iii) the ultra-fine pigment particles must be rapidly dispersed in the medium, (iv) it should be durable; (v) resistant to photochemical reactions because of solar radiation (UV); (vi) weathering, and (vii) it should be economically attractive [3].

The recovery of pigment from coal dump leachate (iron rich mine water) has been studied by neutralization of the leachate with MgO [1]. The Fe^{3+} was removed as $Fe(OH)_3$ and converted into goethite (yellow pigment) through drying of the sludge at 80°C and to hematite (red pigment) at 800°C (**Figure 1**).

The pigments recovered from mine must be tested for their possible use in various applications such as paints and colored concrete products.

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Fig. 1. Pigments recovered by acid mine water treatment

1.2. Objective

This study aimed at the evaluation of performance of pigments recovered from treatment of iron rich mine water for suitability in producing building materials. The specific objectives were to conduct laboratory studies to: (i) evaluate the effect of pigment on the compressive strength of micro-concrete under normal curing and accelerated curing conditions, (ii) evaluate the effect of pigment dosage on the compressive strength, slump and spread of concrete.

II. MATERIALS AND METHODS

A. Materials

Ordinary Portland cement (CEM I 52.5R produced in accordance with SANS 50197 2013), crusher sand, Pigment from current industry supplier, pigment recovered from iron-rich mine water treatment and potable water was used in the test for making concrete specimens.

B. Equipment

The following equipment was used: Weighing scale calibrated to 2kg, mortar mixer, micro-concrete moulds, vibrating table, curing room with bath, Le Chatelier, 100°C oven, setting time machine, and X-Ray Fluorescence (XRF) spectroscope.

C. Procedure

The cement was homogenized, and characterized by testing for the following parameters after 2, 7 and 28 days: (i) compressive strength (in accordance with SANS 50196-1), (ii) setting time, (iii) soundness, and (iv) elemental composition (using X-Ray Florescence spectroscopy). Crusher sand was prepared according to standard preparation procedure of aggregate test samples. They were tested for: (i) water absorption in accordance with SANS 3001, (ii) particle size, (iii) relative density of aggregates SANS 5844, (iv) consolidated bulk density, (v) content of voids in aggregates according to (in accordance with SANS 5845), (vi) fine content-dust, and (vii) sieve analysis of aggregate according to SANS 201. The two pigments were tested for chemical oxide composition using X-ray Fluorescence. Firstly, mixtures of cement, crusher sand and water were combined to produce concrete with no pigment and secondly mixtures were produced which included the pigments. Three concrete samples were compared for performance comparison purposes: (i) Commercial pigment from the South African concrete industry, (ii) pigment recovered from the iron rich mine water, and (iii) concrete without pigment. The pigment was dosed at three content levels, 0%, 3%, 5% and 7% (**Table 2**). Pigments were in line with the recommended dosages of the pigment suppliers. The concretes produced were cured under normal conditions (i.e., in the curing room) and accelerated conditions using the curing chamber using steel mould casting prisms. **Fig.** 2 depicts concrete without pigment and **Fig.** 3 shows cement with pigment. **Fig.** 4 shows prisms in the curing chamber.

Fig. 2. Concrete without pigment

Fig. 3. Concrete with pigment

Fig. 4. Micro concrete prims in curing chamber operated at 90% humidity, 50℃ for 3 hours

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TABLE II: CONCRETE MIX DESIGN FOR PIGMENT PERFORMANCE EVALUATION IN MICRO-CONCRETE

Trial	Cement (g)	Sand (g)	Water (g)	Pigment (g)	Water/ Cement (%)
1	702.00	1330.00	326.00	0.00 (0%)	46.00
2	702.00	1330.00	326.00	21 (3%)	46.00
3	702.00	1330.00	326.00	35 (5%)	46.00
4	702.00	1330.00	326.00	49 (7%)	46.00

The concrete produced was then molded using steel moulds on a vibrating table in order to produce prisms with dimensions 160mm x 40mm x 40mm (Length x breath x height). The concrete was cured for 24 hours in a curing room when cured under normal conditions. The steamed and cured prisms were loaded directly into the curing chamber after mixing. The prisms were removed from the moulds before compressive strength could be tested depending on age. **Fig.5** shows the concrete prisms after demoulding.

Fig.5: Concrete prisms for compressive strength test after 24 hours of curing.

Depending on the compressive strength age test, the demoulded concrete prisms were cured in a curing bath.

D. Analytical procedure

The cement and pigment were analyzed for elemental composition using X-Ray Fluorescence spectroscopy, the concretes produced with and without pigment were tested for compressive strength after 3 hours of steam curing); 1, 3, 7 and 28 days of normal curing. The slumps, indicating the workability of concrete produced, were also noted.

III. RESULTS AND DISCUSSION

A. Raw Materials

1) Cement

Table 3 shows that the cement used was compliant with 52.5R performance as per SANS 197-1 (2013) as the 2 days and 28 days compressive strength were more than the target values of 30MPa and 52.5MPa. The differences between the actual and target values were 4.3MPa and 9.33MPa, respectively. The initial setting times and soundness were also compliant at 146.67 minutes and 1 mm against a target of $\geq$ 45 minutes and $\leq$ 10 mm, respectively. **Table 4** shows that the actual elemental composition for CaO, SiO_2, Al_2O_3 and Fe_2O_3 was within the required ranges. The chloride content was within a target of less than 0.1%. **Table 5** showed that only 0.56% did not pass through a 45µm sieve. The average SSA was 445 cm/g and the density was 2.98 g/cm^3.

2) Pigment

The elemental composition of iron rich water pigment had Fe_2O_3 that was less than the current market supplier pigment by 12.8%. The Fe_2O_3 concentration is responsible for intensity of the red color in the concrete. This was evident as the color of the iron rich water pigment was not intense compared to that of current market suppliers. Pigments from iron rich mine water had significant contents of Al_2O_3 which is responsible for rapid setting of cement. The total alkalis, as Na_2O (XRF) were 0.76% and 0.02% for iron rich mine water pigment and pigment from a current market supplier, respectively (**Table 6**). Total alkali content limit in cement should be $\leq$ 0.6%. High alkali in cement results in early compressive strength development and reduces late compressive strength. High alkalis in concrete results in an alkali-silica reaction, reduction in workability, and reduction in compressive strength. **Table 7** shows that the density of the mine water pigment was similar to pigment available on the market.

3) Crusher sand

Table 8 shows the results of grading analyses of crusher sand used. The sand was well graded as indicated by the green line between the lower and the upper limits. The sand had low water absorption and dust content indicating good suitability for concrete production.

B. Effect of pigment for producing colored concrete

Table 9 compared the compressive strength, slump and spread of concrete for: (i) no pigment, (ii) mine water pigment and (iii) commercial pigment for different pigment dosages (3%, 5%, 7%). It was noted that: (i) more colour with increased pigment dosage, (ii) increased compressive strength with increased pigment dosage, (iii) reduction in slump and spread with increased pigment dosages (iv) mine water pigment performed better than market pigment in the case of compressive strength and colour and less effective with respect to slump and spread.

Table 10 shows colored concrete steam cured at 90% humidity and 50°C for 3 hours. Increased pigment dosages resulted in in an increase in compressive. In the case of current market pigment, increased pigment dosages resulted in a reduction in compressive strength of concrete.

TABLE III: COMPRESSIVE STRENGTH AND SETTING TIME

Trial	Compressive strength (MPa)			Setting time			
	2 day	7 days	28 days	Initial set (Min)	Final set (Min)	Consis-tency (%)	Expan-sion (mm)
1	33.90	46.20	61.8	148.00	214.00	30.58	1.00
2	34.25	47.20	61.8	148.00	214.00	30.58	1.00
3	34.75	46.50	61.9	144.00	211.00	30.58	1.00
Ave	34.30	46.63	61.83	146.67	213.00	30.58	1.00
Target	30		52.5	>45			<10.0
Difference	4.3		9.3	101.67			9.0

TABLE IV: ELEMENTAL ANALYSIS WITH XRF

Determinant	Units	Value	
		Actual	Required
SiO_2	%	20.55	20 - 23
Al_2O_3	%	4.85	4 - 6
Fe_2O_3	%	3.10	2 - 4
CaO	%	61.79	60 - 68
MgO	%	2.34	
K_2O	%	0.17	
Na_2O	%	0.09	
TiO_2	%	0.49	
Mn_2O_3	%	0.26	
P_2O_5	%	0.09	
Cr_2O_3	%	0.03	
SrO	%	0.00	
SO_3	%	2.94	
Cl^-	%	0.046	<0.100
LOI @ 950		3.50	
Sum	%	100.21	

TABLE V: FINENESS AND DENSITY

Trial	Fineness		Density
	Retainment on 45 µm sieve (%)	SSA (Blaine) (cm^2/g)	(g/cm^3)
1	0.56	445.0	2.98
2	0.55	443.0	2.98
3	0.56	446.0	2.98
Average	0.56	444.7	2.98

TABLE VI: ELEMENTAL ANALYSIS WITH XRF

Determinant	Unit	Iron rich mine water pigment	Conventional market supplied pigment
SiO_2	%	0.76	0.00
Al_2O_3	%	6.14	0.16
Fe_2O_3	%	91.36	104.18
CaO	%	0.27	0.11
MgO	%	0.09	0.00
K_2O	%	0.00	0.00
Na_2O	%	0.76	0.02
TiO_2	%	0.01	0.23
Mn_2O_3	%	0.28	0.06
P_2O_5	%	0.00	0.00
SrO	%	0.00	0.01
SO_3	%	0.83	0.00
LOI @ 950		4.44	2.41
Sum	%	104.96	107.24

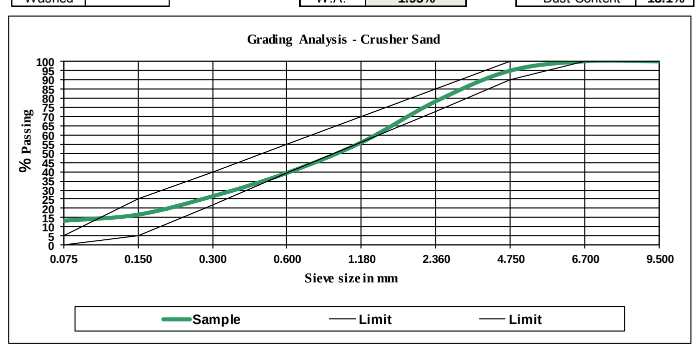
TABLE VII: DENSITY

Type of pigment	Density (g/cm^3)
Currently supplied to the market	4.98
Iron mine water pigment	4.66

TABLE VIII: GRADING ANALYSIS

Sieve size mm	Mass Retained	% Retained	Cum. % Retained	% Passing	% Passing Specification
9.5	**0.0**	0.0	0.0	100.0	100
6.7	**0.0**	0.0	0.0	100.0	100
4.75	**32.0**	5.2	5.2	94.8	95-100
2.36	**104.0**	16.7	21.9	78.1	
1.18	**139.0**	22.4	44.3	55.7	
0.6	**103.0**	16.6	60.9	39.1	
0.3	**79.0**	12.7	73.6	26.4	
0.15	**62.0**	10.0	83.6	16.4	5 - 25
0.075	**20.5**	3.3		13.1	0 - 10
Pan	**31.5**				
Pan	**50.0**				
Dry Mass Washed	571.0			W.A. =	**1.95%**

Wet Mass =	**621**
Dry Mass =	**621.0**
LBD (kg/m^3) =	**1643**
CBD (kg/m^3) =	**1844**
RD =	**2.66**
F.M. =	**2.89**
% Moisture =	**0.00%**
Dust Content=	**13.1%**



IV. Conclusions

Pigment recovered from treatment of iron rich mine water can be used to produce colored concrete using Ordinary Portland Cement (CEM I) 52.5R; crusher sand and water suitable for manufacturing concrete.

The suitable dosage of pigment is between 3% and 7%.

Acid mine contains high concentrations Fe^{3+} can be recovered as $Fe(OH)_3$, and processed to pigment.

This study revealed: (i) More intense colour was produced with an increase in pigment dosage; (ii) increased compressive strength was achieved with an increase in pigment dosage; (iii) reduction in slump and spread happened with increased pigment dosages, and (iv) mine water pigment performed similarly to commercial pigment in the case of compressive strength and spread but poorer in the case of slump.

TABLE IX: CONCRETE PERFORMANCE RESULTS AT NORMAL CURING CONDITIONS

Trial	**Compressive strength (MPa)**				**Slump (mm)**	**Spread (mm)**
	1 day	3 days	7 days	28 days		
Concrete with 0% pigment	30.09	47.54	51.69	74.41	35.00	110.00
Concrete with 3% Iron mine water pigment	30.22	48.35	56.96	77.23	25.00	100.00
Concrete with 3% Industry supplier pigment	26.65	48.33	63.01	75.58	45.00	105.00
Concrete with 5% Iron mine water pigment	30.91	46.13	59.04	79.80	20.00	90.00
Concrete with 5% Industry supplier pigment	28.33	46.00	59.91	79.53	35.00	100.00
Concrete with 7% Iron mine water pigment	31.79	49.93	59.32	77.48	5.00	90.00
Concrete with 7% Industry supplier pigment	28.23	50.32	60.53	76.93	25.00	90.00

Slump indicates the workability of concrete.
Spread indicates the flow-ability of concrete.

V. RECOMMENDATIONS

Further studies should be conducted to determine the color stability of concrete produced using pigment recovered from iron rich mine water. This would be to assess the resistance to photochemical reactions that occur when exposed to solar radiation (UV) and weathering.

Concrete performance results at steamed cured at 90% humidity, 50 ℃ for 3 hours

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TABLE 10: CONCRETE PERFORMANCE RESULTS (STEAMED AND CURED AT 90% HUMIDITY, 50℃ FOR 3 HOURS)

Trial	**Compressive strength (MPa)**	**Slump (mm)**	**Spread (mm)**
Concrete with no pigment	3.88	35.00	110.00
Concrete with 3% Iron mine water pigment	4.50	25.00	100.00
Concrete with 3% Industry supplier pigment	3.24	45.00	105.00
Concrete with 5% Iron mine water pigment	4.13	2.00	90.00
Concrete with 5% Industry supplier pigment	2.69	35.00	100.00
Concrete with 7% Iron mine water pigment	5.27	5.00	90.00
Concrete with 7% Industry supplier pigment	3.56	25.00	90.00

REFERENCES

[1] Letjiane, S. L., Maree, J. P., Onyango, M. S. & Adeniyi, A., 2019. *Pre-treatment of coal dump leachate with MgO for pigment recovery.* Perm, Russia, International Mine Water Association, pp. 101-106.
[2] Sulcova , P., 2012. Options synthesis and application testing of inorganic pigments, . In: *Zborník príspevkov zo VII. konferencie s mezinárodnou účasťou Partikulárne látky vo vede.* s.l.:s.n., p. 250–254
[3] Margoldova, J., 2010. Colored, not only grey concrete. *Materialy a Technologie*, Volume 1, pp. 32-36.
[4] SANS 50196-1, 2013. Methods of testing cement. Johannesburg: SABS Standard Division.
[5] SANS 50197-1, 2013. Composition, specifications and conformity criteria for common cements. Johannesburg: South African National Standards (SANS). *Materialy a Technologie,* Volume 1, pp. 32-36.
[6] SANS 3001. Determination of the bulk density, apparent density and water absorption of aggregate particles retained on the 5 mm sieve for road construction materials. Johannesburg. SABS Standard Division.
[7] SANS 5845, 2012. Method for determining the uncompacted bulk densities and the voids content of an aggregate. Johannesburg: SABS Standard Division.
[8] SANS 5844, 2012. Particle and relative density of aggregates. Johannesburg: SABS Standard Division.
[9] SANS 201, 2012. Sieve Analysis, fines content and dust content of aggregates. Johannesburg: SABS Standard Division.

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