

Portland cement production using mineral wastes

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PORTLAND CEMENT PRODUCTION USING MINERAL WASTES

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ABSTRACT

A Type I Portland cement has been produced using anorthite from copper-nickel tailings and raw taconite tailings. The cement exhibited better strength properties than ordinary Type I Portland cement and gave a stronger concrete when tested under identical curing conditions. Factors leading to the attainment of these higher strength values are identified and their effects on the ultimate mechanical properties of cement are discussed. It is also anticipated that the compositional variety of tailings may also have other beneficial effects on long-term cement behavior such as resistance to sulfate attack.

Introduction

This paper describes the development of Portland cement from a non-conventional raw feed composed of copper-nickel tailings as a replacement to argillaceous components in a conventional cement feed.

Limestone and iron bearing taconite tailings are used as calcareous and ferruginous components, respectively.

Background

In northern Minnesota lie vast deposits of copper-nickel ore known as the Duluth gabbro which are estimated to contain 28 million metric tonnes of copper and 8 million metric tonnes of nickel (1).

In the event of the development of these deposits a large amount of tailings, exceeding 90% of the bulk ore, will be produced containing among other discarded minerals, some amount of finely disseminated fibrous amphiboles as a potential pollutant of water and air, thus presenting both disposal and pollution problems in close proximity to an environmentally sensitive location known as the Boundary Water Canoe Area (2).

The mineralogical composition of these tailings, given in Table 1,

TABLE 1

Mineralogical Composition of the Copper-Nickel Tailings (% Wt.)

| | |
|--|-------|
| Plagioclase | 43.03 |
| Olivine | 19.54 |
| Pyroxene | 18.18 |
| Biotite | 3.18 |
| Opauques (ilmenite, magnetite, Cu-Ni sulfides) | 9.55 |
| Locked Particles | 1.33 |

identifies, however, that these tailings can be a source of some useful minerals, particularly the plagioclase which constitutes over 43% of the tailings. Plagioclases are a unique source of aluminosilicates and have among other uses a possible direct use as argillaceous components in the manufacturing of hydraulic cements. By so doing it will not only introduce a new source of raw feed for cement - a commodity which is currently not produced in Minnesota - but also reduce the disposal problem of the tailings.

Ferruginous additive needed for the cement raw feed will be provided by another tailing source - the iron bearing taconites - which are also present in large amounts in the adjacent areas of Northern Minnesota.

The present investigation is therefore aimed at making use of these tailings in order to develop hydraulic cement and critically testing the products to assess engineering behavior.

Plagioclase as a Component for Cement Feed

Conventionally a hydraulic cement is obtained by heating to 1450°C a ground mixture of limestone and clay or other mixture of similar composition (3) and intergrinding the resulting clinker with a small proportion of gypsum.

The copper-nickel tailings, when upgraded to plagioclase (anorthite) have a chemical composition close to that of a clay used in cement making, i.e., it is an aluminosilicate of the lime type. A typical plagioclase concentrate obtained from the Cu-Ni tailing contains nearly 57% SiO₂ and 27% Al₂O₃ identifying it to be a prime source for silica and alumina. A detailed analysis is given in Table 2.

TABLE 2

Chemical Composition of Plagioclase Concentrate (Anorthite) (% Wt.)

| SiO ₂ | Al ₂ O ₃ | CaO | Fe ₂ O ₃ | MgO | Na ₂ O | K ₂ O | SO ₃ |
|------------------|--------------------------------|------|--------------------------------|------|-------------------|------------------|-----------------|
| 56.40 | 27.10 | 8.80 | 0.62 | 0.16 | 4.5 | 0.81 | 0.0 |

Some earlier attempts have already shown the use of anorthites in the development of white Portland cement (4,5) and their potential in new high temperature cementing materials (6).

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It may be pointed out that both these tailings are available in ground form requiring little of the further grinding otherwise needed in conventional cement feed preparation.

Materials and Methods

Copper-nickel tailings received as such were upgraded in anorthite by methods involving gravity and magnetic separation (1,7). Taconite tailings were obtained from the Erie Company, Hoyt Lakes, Minnesota (8) and their fractions finer than 200 mesh collected. A mixture of both these tailings along with limestone to produce a Type I cement clinker was made with the following proportions: limestone (74.6%); anorthite (12.5%); taconite tailings (10.9%) and anhydrite (2.0%) (3).

An amount of 2.0 % anhydrite was added in the clinker feed to reduce the formation of alkali aluminate phase in the clinker due to the presence of excessive Na_2O (4.5%) in anorthite. A detailed chemical analysis of the clinker feed is given in Table 3.

TABLE 3

Chemical Analysis of the Clinker Feed

| | Material Description | | | |
|-------------------------|----------------------|----------------------|-----------|-----------|
| | Anorthite | Taconite Tailings | Limestone | Anhydrite |
| SiO_2 | 56.96 | 58.54 | 2.17 | - |
| Al_2O_3 | 27.57 | 0.64 | 0.13 | - |
| Fe_2O_3 | 0.62 | 27.40 | 0.37 | - |
| CaO | 8.80 | 4.40 | 53.96 | 41.20 |
| MgO | 0.16 | 3.10 | 0.33 | - |
| SO_3 | 0.18 | 0.23 | 0.00 | 58.80 |
| L.O.I. | 0.40 | 5.69 | 42.92 | - |
| Na_2O | 4.50 | - | 0.03 | - |
| K_2O | 0.81 | - | 0.06 | - |
| TiO_2 | - | - | 0.03 | - |
| P_2O_5 | - | - | - | - |
| Total | 100.00 | 100.00 | 100.00 | 100.00 |

Any Na_2O present without a sulfate balance can produce an alkali aluminate phase which may cause setting problems. Target amounts of clinker phases to

produce a Type I cement clinker using cement chemists notation* were determined to be as follows: C_3S (55-60%); C_2S (20-22%); C_3A (8-10%) and C_4AF (8-10%).

Preparation and Firing of Clinker Feed

The limestone was ground in a ball mill until 85% was passing a 200 mesh sieve. Anorthite and taconite tailings were already very fine and therefore required little grinding. The three components along with anhydrite were thoroughly mixed prior to pelletizing with water for the rotary kiln burning. Raw feed (1/4 to 1/2 inch pellets) was fed into a 15-ft. long and 5-in. wide pilot plant rotary kiln, fired with natural gas as fuel to a burning temperature of 1450-1480 C with an oxygen level in the kiln at 1.5-2.0%. The fired clinker was cooled and collected for testing.

Analytical Evaluation of the Clinker

Qualitative X-Ray diffraction analysis shows that the clinker produced from the feed is of quality grade and the levels of phases estimated from the peak intensities are similar to those of target values (see Table 4).

TABLE 4

Estimated Phase Levels (% Wt.) from XRD Analysis

| C_3S | C_2S | C_3A | C_4AF | Free CaO | MgO | Alkali Aluminate |
|--------|--------|--------|---------|-------------|-----|---------------------|
| 55-60 | 20-22 | 8-10 | 8-10 | < 1 | < 1 | none |

Optical analysis of the clinker confirms its quality to be from good to excellent and shows (as in Figure 1) a distribution of well formed medium sized C_3S crystals and clusters of rounded striated C_2S crystals. C_4AF is present as white bright area in the interstices and medium sized C_3A crystals are also uniformly distributed. Only traces of CaO and MgO are found whereas alkali sulfates are very rarely present. The clinker also shows good porosity (as the large grey areas in the photomicrograph) allowing easy grinding. The quality of the clinker predicts good strength development.

Chemical and Physical Testing

The clinker was interground with 5% gypsum to a Blaine fineness of 3500 cm^2/g to form the cement used in chemical and physical tests.

Chemical analysis and calculated compound composition of major phases of the cement produced an oxide composition with the presence of only 0.24% Na_2O (see Table 5).

The analysis shows the cement to be of good quality from which the production of strong and sound concrete is predicted.

*C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3

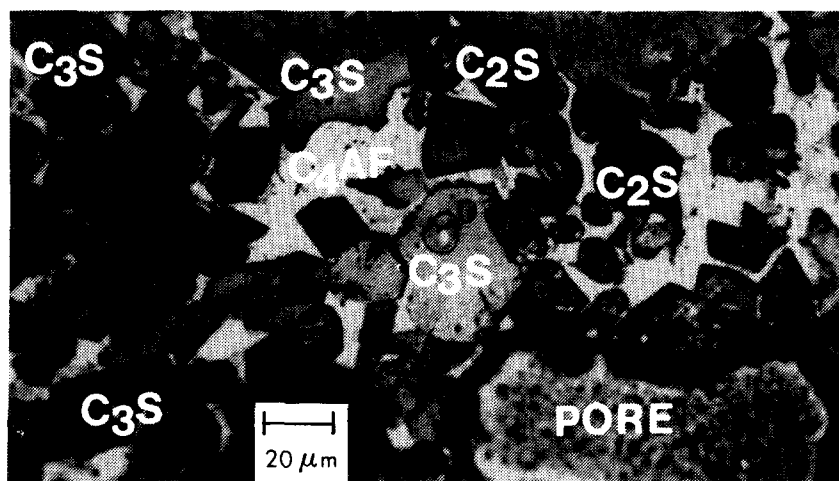


FIG. 1

Photomicrograph of the clinker showing well formed C_3S crystals; C_2S crystals occurring in clusters; C_4AF occurring in the interstices; C_3A well distributed within the interstices; CaO and MgO in traces.

TABLE 5

| I. Chemical Analysis of Cement (% Wt.) | | | |
|---|--------|-------------------|---------|
| SiO ₂ | 20.71 | Na ₂ O | 0.24 |
| Al ₂ O ₃ | 5.07 | K ₂ O | 0.03 |
| CaO | 64.01 | SO ₃ | 2.30 |
| Fe ₂ O ₃ | 4.63 | TiO ₂ | 0.06 |
| MgO | 0.86 | L.O.I. | 1.46 |
| II. Calculated Compound Composition of Major Phases (% Wt.) | | | |
| C_3S | C_2S | C_3A | C_4AF |
| 56 | 17 | 6 | 14 |

According to the ASTM C150 specifications (9) for Type I cements, a series of physical tests were conducted on the cement to determine its soundness; setting time (initial and final); fineness; air content; false set and compressive strength. Results are shown in Table 6.

Tests for compression strength on some concrete specimens (2.5" cubes at w/c = 0.49) and for flexural strength on mortars prisms (1" x 1" x 6" at w/c = 0.49) both prepared from the cement were also conducted. Details of the results are given in Table 7 and Figures 2 and 3.

TABLE 6

| Results from Physical Test on the Cement Produced from Tailings | | |
|---|---------------|---|
| Test Results | | ASTM Specifications C 150-83a Type I |
| Setting Time (Vicat) | | |
| Initial | 2 hr. 20 min. | Not less than 45 min & not more than 6 hr, 15 min |
| Final | 4 hr. 30 min. | Not more than 8 hr (C150-78a) |
| Soundness (Expansion) | 0.03% | Maximum 0.80% |
| Fineness (Blaine) | 3540 Sq. cm/g | Minimum 2800 Sq.cm/g |
| Fineness by #325 Sieve | 93.6% passing | Not specified |
| Air Content | 9.8% | Maximum 12.0% |
| False Set (Paste Method) | 75% | Minimum 50% |
| Compressive Strength - | | |
| 1 day test | 1600 psi | - |
| 3 day test | 3250 psi | Minimum 1800 psi |
| 7 day test | 5100 psi | Minimum 2800 psi |
| 28 day test | 8150 psi | Minimum 4000 psi |
| 110 day test | 10350 psi | - |

TABLE 7

| Flexural Strength and Compressive Strength Values (PSI) for Mortar and Concrete Specimens, Respectively, Made from the Cement Mortar 1" x 1" x 6" Prism and Concrete 2.5" x 2.5" x 2.5" Cubes; at W/C =0.49. | | | | | |
|--|-------|-------|-------|-------|-------|
| Curing Time (Days) | 1 | 3 | 7 | 28 | 110 |
| Flexural Strength (Mortars) | 306 | 560 | 740 | 820 | 950 |
| Compressive Strength (Concrete) | 1,500 | 3,200 | 5,000 | 7,100 | 8,900 |

Analysis of Data

Results from the physical tests show that the cement adequately meets the ASTM requirement for a Type I cement except that the compressive strength values on the neat cement pastes are approximately double the required minimum values (see Table 6).

FIG. 2

Development of compressive strength of concrete specimen made from:

the tailing cement ▲
 Type I Portland cement ●
 at w/c = 0.49

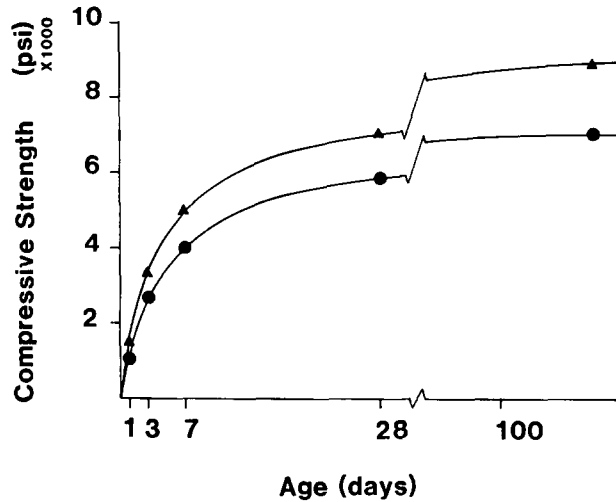
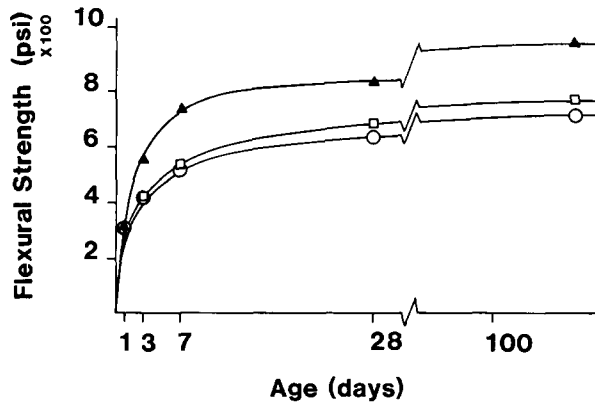


FIG. 3

Development of flexural strength of mortar specimen made from the tailing cement ▲ ; and variation of calculated flexural values obtained from compressive strengths of the tailing cement □ and concrete ○ using equation 1.



Compression tests on concrete specimen made from the cement also show higher strength development leading to high ultimate strengths when compared to similar specimen from Type I cement tested under identical conditions (see Figure 2 for strength comparisons).

The reason for strength gain may be attributed to the presence of relatively high C_3S content in the cement giving a high C_3S/C_2S ratio of 3.29 as compared to an average of 2.01 for a Type I cement (10). A list of the compound compositions of some Type I cements, given in Table 8, shows that the C_3S/C_2S ratio varies with composition from 0.94 to 3.06. The C_3S compound has higher strength rates than C_2S , and if present in excess, contributes dominantly towards higher strength values in the early periods of hydration. Both C_3S and C_2S are, however, primarily responsible for strength development of cement. An approximate assumption is that C_3S contributes more to the strength gain during the first month and C_2S influences the strength development from one month onward (11,14).

The presence of C_4AF in the cement is also relatively higher; 14% as compared to an average 7.5% for Type I cements. This would, however, contribute little towards the strength development (12). C_4AF on its own

TABLE 8

Major Compound Composition (% Wt.) and C_3S/C_2S Ratios for Various Type I Cements.

| Type I Cements | C_3S | C_2S | C_3A | C_4AF | C_3S/C_2S Ratio |
|------------------------|--------|--------|--------|---------|-------------------|
| 1 | 55 | 18 | 11 | 7 | 3.06 |
| 2 | 54 | 23 | 9 | 6 | 2.35 |
| 3 | 47 | 28 | 7 | 9 | 1.68 |
| 4 | 33 | 35 | 14 | 8 | 0.94 |
| Mean C_3S/C_2S Ratio | | | | | 2.01 |
| Tailing Type I Cement | 56 | 17 | 6 | 14 | 3.29 |

hydrates faster, but in the presence of gypsum, which is generally added to prevent a flash set caused by a violent hydration reaction by C_3A during mixing of the cement, it will have a regulated setting behavior (13). Again, a high C_4AF value combined with a low value of C_3A , 6% by weight, is generally regarded to be useful as it lessens the amount of C_3A hydration products, particularly the monosulfoaluminates which are prone to sulfate attack (14).

A common concept is that C_3A in the presence of gypsum hydrates to calcium sulfoaluminates known as "ettringite." If the sulfate ions are all consumed before the C_3A has completely hydrated, the ettringite transforms to monosulfoaluminates which when brought into contact with a new source of sulfate ions reform to ettringite once again. This reforming of ettringite is the basis for attack when exposed to fresh sulfate ions. With cements low in C_3A but high in C_4AF content, the formation of ettringite from monosulfoaluminates does not occur. It may be that iron-substituted monosulfoaluminate cannot react to form ettringite or that the presence of amorphous hydrous oxides of iron and aluminate, which do form during sulfate reaction, may in some way prevent the completion of ettringite formation (14,15,16).

Another important engineering property of cement is its bonding behavior which is commonly assessed by its flexural strength. Results from flexural tests on the cement, given in Table 9, show that the cement possesses excellent bonding properties. For instance, a 28 day flexural strength for cement mortar is 820 psi as compared to calculated flexural values of 632 psi and 677 psi for concrete and neat pastes, respectively. These calculated flexural values are based on a generalized correlation that exists between the flexural and compressive strength as

$$\sigma_f = 7.5 (\sigma_c)^{1/2} \quad (1)$$

where σ_f is the flexural strength and σ_c is compressive strength (14).

Variations of observed and calculated flexural values with curing times are also given in Figure 3.

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TABLE 9

Comparison of Observed Flexural Strength (σ_f) with the Calculated Flexural Strength from Compressive Strength Values (σ_c of both Cement and Concrete Specimens Using Equation 1.

| Curing Times (Days) | 1 | 3 | 7 | 28 | 110 |
|---|-----|-----|-----|-----|-----|
| Observed Flexural Strengths | 306 | 560 | 740 | 820 | 950 |
| Calculated from Cement Compressive Strength | 300 | 428 | 536 | 677 | 763 |
| Calculated from Concrete Compressive Strength | 290 | 424 | 530 | 632 | 708 |

Another check on the flexural strength is that the ratio of flexural to compression strength should range from about 0.11 to 0.23 (14,17) which holds true for calculated mean ratios of 0.14 and 0.15 recorded both for mortar to cement and mortar to concrete, respectively (see Table 10). Calculated ratios for fresh specimens are however higher; 0.19 and 0.20, respectively, for 1 day old specimens, indicating that the cement acquires better bonding strength in the early ages, but compressive strength dominates as the hydration progresses, yielding a much higher ultimate strength, as referred to above.

TABLE 10

Ratios of Observed Flexural Strengths to Compressive Strength (σ_f/σ_c) from both Cement and Concrete Specimens

| Curing Time (Days) | 1 | 3 | 7 | 28 | 110 | Mean |
|---------------------------------------|------|------|------|------|------|------|
| σ_f/σ_c (for cement) | 0.19 | 0.17 | 0.15 | 0.10 | 0.09 | 0.14 |
| σ_f/σ_c (for concrete) | 0.20 | 0.18 | 0.15 | 0.12 | 0.11 | 0.15 |

Conclusions

The utilization of copper-nickel and taconite tailings as a partial replacement of raw feed for cement making is practically possible. The cement thus produced exhibits excellent strength properties; adequately meets the required standard specifications and can have marketable potential at least in the state of Minnesota which currently produces no cements.

This approach of tailing consumption could also simultaneously reduce the impact of tailing disposal around the environmentally sensitive area of northern Minnesota.

In this work approximately 24% of the raw feed for the cement is derived from tailings. Whether this proportion can further be increased without significantly effecting the cement properties is a matter of further investigation.

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References

1. I. Iwasaki, K.A. Smith and A.S. Malicsi, "By-product Recovery from Copper-Nickel Bearing Duluth Gabbro," Report for the U.S. Dept. of the Interior Mineral Institute, U.S. Bureau of Mines, Washington, D.C. 20241, MRRC, 56 East River Road, Mpls, MN 55455 (1982).
2. "Regional Copper-Nickel Study," The Minnesota Environmental Quality Board (1979).
3. J. Skalny and K.E. Daugherty, "Everything You Always Wanted to Know about Portland Cement," p. 38, Chemtech (January, 1972).
4. L.A. Zakharov, "Anorthosites - New Raw Material for Preparing White Cement," *Tsement* 10, p. 12 (1969).
5. Rajeswara, A.V. Rao, et al. "White Cement from Sittampundi Anorthite," *Trans. Indian Ceram. Soc.* 20, p. 7 (1961).
6. D.M. Roy, E.L. White, C.A. Langton and M.W. Grutzeck, "New High Temperature Cementing Materials for Geothermal Wells: Stability and Properties," Final Report, Material Research Laboratory, The Pennsylvania State University, PA 16809 (July 1980).
7. I. Iwasaki, A.S. Malicsi, R.J. Lipp and J.S. Walker, "By-Product Recovery from Copper-Nickel Bearing Duluth Gabbro," *Resources and Conservation*, 9, p. 105, Elsevier Scientific Publishing Co., Amsterdam (1982).
8. D.K. Clyde, The Erie Mining Company, Box 847, Hoyt Lakes, Minnesota.
9. ASTM C150 "Standard Specification for Portland Cement," American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103 (1983).
10. F.M. Lea, *The Chemistry of Cement and Concrete*, Chemical Publishing Company, Inc., New York (1971).
11. A.M. Neville, *Properties of Concrete*, Pitman Publishing Ltd., London, (1981).
12. J. Bensted, "Hydration of Portland Cement," *Advances in Cement Technology*, p. 307, Ed: Ghosh, Pergamon Press Ltd., Oxford (1983).
13. G. Frigione, "Gypsum in Cement," *Advances in Cement Technology*, p. 485, Ed: Ghosh, Pergamon Press Ltd., Oxford (1983).
14. S. Mindess and J.F. Young, *Concrete*, Prentice-Hall, Inc., Englewood Cliffs (1981).
15. W.C. Hansen, "The Chemistry of Sulphate Resisting Cements," *Performance of Concrete*, Ed: Swenson, University of Toronto Press (1968).
16. K. Mather, "Test and Evaluation of Portland and Blended Cements for Resistance to Sulfate Attack," *Cement Standards-Evolution and Trends*, p. 74, ASTM STP663, Ed: P.K. Mehta, ASTM (1978).
17. G.E. Troxell, H.E. Dans and J.W. Kelly, "Composition and Properties of Concrete," McGraw Hill, Civil Engineering Series, McGraw-Hill, Inc. (1968).