Conversion of Coal Prep-Wastes into Portland Cements

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ABSTRACT

A developmental project was carried out to explore the potential for the economic use of coal-prep waste. Coal prep-wastes were used as a component of raw feed in producing portland cement clinker.

Several combinations of prep-wastes, and cement kiln dust and raw materials from different Illinois cement plants were tested in the laboratory to generate clinkers. The raw mixes were fired at $1400^{o}C$ as compared to $1450^{o}C$ usually required for commercial clinker production.

The clinkers were ground to cement fineness and were blended with an equal portion of ordinary portland cement to produce test cement samples for evaluation. When tested for compliance with ASTM C 150 specification, these cements showed properties comparable with those of commercially produced cements.

KEYWORDS: Coal-prep-waste, cement kiln dust (CKD), fuel supplement, cement manufacturing, cement raw feed component, cement testing, clinker evaluation, sulfates, alkalies, calcium langbeinite, gypsum

INTRODUCTION

More than 5 million tons of prep-wastes are generated annually from coal-processing plants in Illinois. Except for occasional use as mining back fill, these wastes have not found a beneficial reuse. These prep-wastes are routinely disposed of in landfills and the accumulation of these wastes over the years must have amount to several hundred million tons. At the same time, cement plants in Illinois generate about 150,000 tons of cement kiln dust (CKD) each year. Although a bulk of the CKD is recycled with the plant raw feed, large amounts of alkali-rich CKD still remain accumulated in the landfills, where they can potentially leach into the ground and cause environmental imbalance.

Since the prep-wastes are typically composed of silica, alumina, iron oxide, sulfur, and residual coal – a composition similar to clay and shale used in cement manufacture – the prep-wastes appear to be a suitable substitute for

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cement raw feed. Appropriate amounts of alkali-rich CKD would be added to the raw mix for the alkalies to react with sulfur in the prep-waste to form sulfates and retained in clinker. Whereas, the presence of residual coal (about 25% based on the loss on ignition, L.O.I.) in the prep-wastes will provide supplementary fuel during the clinker firing.

By virtue of their reactive nature, prep-wastes are also expected to enhance combinability with lime and form cement clinker at a reduced temperature. This would result in energy conservation and improved production during the cement manufacturing process. It is further anticipated that the sulfate compound formed in clinker will be calcium langbeinite, which has a set regulating effect similar to gypsum in ordinary portland cement. This would preclude the need for adding gypsum (a purchased material) during finish grinding.

A number of raw mixes were prepared with prep-wastes from local coal-processing plants, and CKDs and raw materials from Illinois cement plants. Use of prep-wastes was maximized in replacing shale, clay, sand, and mill-scale. The most promising clinkers were ground, blended with ordinary cement, and evaluated as per ASTM C 150 specification.

MATERIAL REPARATION AND EXPERIMENTAL PROCEDURES

Several samples of prep-wastes were collected from Illinois coal-processing plants, including those in close proximity to the cement plants. Likewise, samples of CKD and typical raw materials (limestone, shale, clay, sand, mill-scale, etc.) from cement plants were also procured. These materials were analyzed for their chemical composition using X-ray fluorescence (XRF) technique. Results are given in Table 1. As can be seen that the prep-wastes were rich in SiO_2, Al_2O_3, Fe_2O_3, and CaO, confirming their appropriateness for use as substitute for clay or shale in cement raw feed.

Table 1. Composition of coal prep-wastes and cement kiln dusts, wt. %

Analyte	Prep-wastes from coal-processing plants				Cement kiln dusts from cement plants		
	Prep-waste 1	Prep-waste 2	Prep-waste 3	Prep-waste 4	CKD 1	CKD 2	CKD 3
SiO_2	27.38	21.28	43.24	46.33	10.77	17.41	15.83
Al_2O_3	9.82	5.69	11.17	13.76	2.92	6.65	4.56
Fe_2O_3	12.63	15.78	9.6	3.79	1.46	2.15	1.77
CaO	17.0	12.32	3.8	0.63	33.42	39.22	42.84
MgO	0.67	0.04	1.13	1.06	1.87	1.78	1.47
SO_3	5.26	15.07	3.25	0.32	8.01	1.15	11.21
Na_2O	0.4	0.22	0.74	2.29	0.22	0.38	0.57
K_2O	1.18	0.76	2.04	0.73	9.89	1.06	4.31
L.O.I.	24.5	26.63	23.94	30.27	27.98	29.72	15.21

The prep-wastes may also contain significant amounts of sulfur (shown as SO_3). The loss on ignition (L.O.I.) values for most prep-wastes were around 25%. CKDs were typically rich in CaO, alkalies, SiO_2, and also sulfates. Alkalies were required in the mix design to tie up sulfur from the prep-wastes.

The prep-wastes were also tested by differential scanning calorimetry (DSC) to determine the fuel value as well as the temperature of volatilization of any combustible organics present. Selected DSC plots for the prep-wastes are shown in Figures 1 and 2.
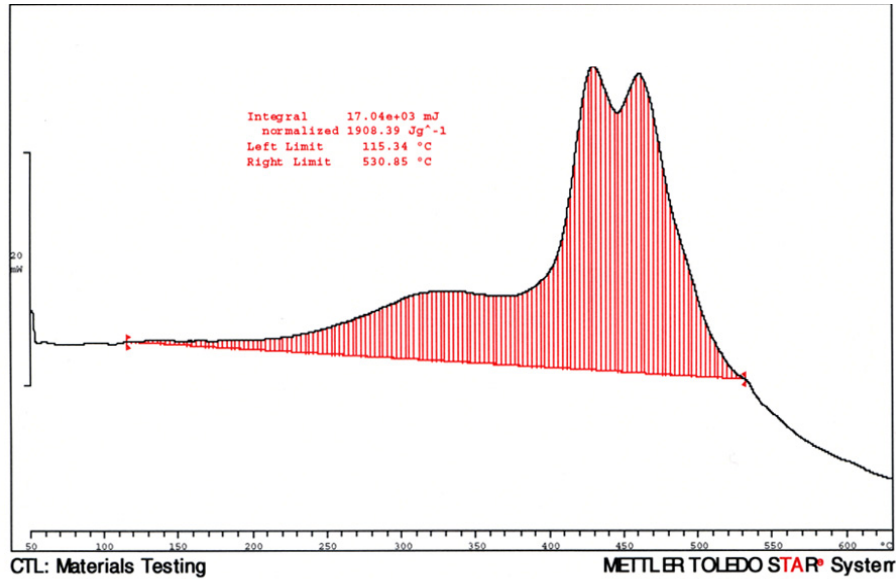
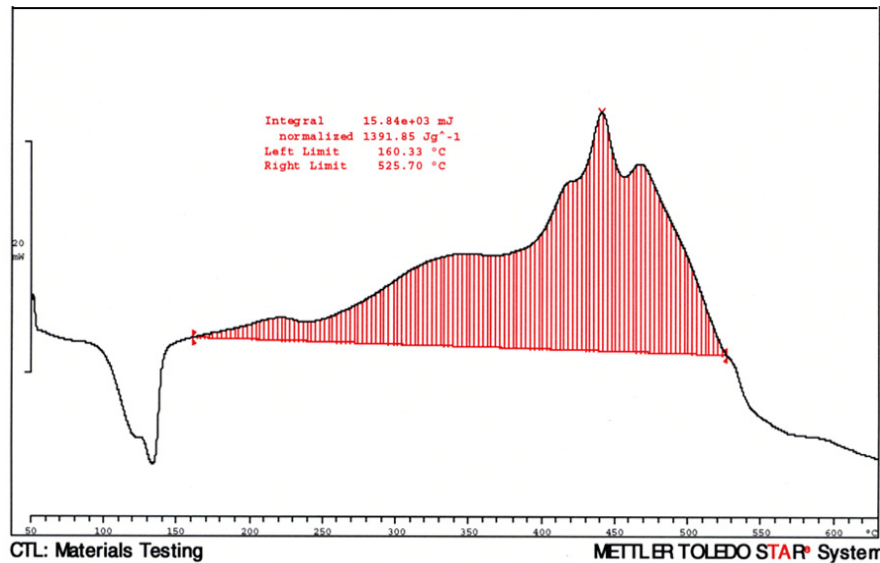**Figure 1. DSC plot showing exothermic peaks for a prep-waste sample**

Figure 2. DSC plot showing exothermic peak for another prep-waste sample

Exothermic peaks starting from 350°C indicate a heat release by combustion of residual coal in the prep-wastes. However, small peaks at lower temperatures indicate the presence of volatile combustible components in the wastes. Since these materials may be released at low temperatures, they may escape combustion in cement kilns as unburned volatile organic compounds (VOCs) and cause emission problems.

Raw Mix Formulations
Prep-wastes with a L.O.I. of around 25% and CKDs with high alkali contents were selected for raw mix preparation. The use of prep-waste was maximized as the principal source of alumina, silica, and iron. Insofar as possible within compositional constraints, the mix consisted of prep-wastes, CKD, and limestone only. The use of prep-waste and CKD was maximized. However, where necessary, minor amounts of corrective materials such as shale, clay, and sand were added to adjust the lime saturation factor, silica modulus, and other cement production parameters.

Based on mix composition and firing conditions tested, the two best raw mix formulations were selected for clinker production. Again, the use of prep-wastes and CKD was maximized. The material combinations of the final two mixes designated as "Raw Mix I" and "Raw Mix II" are shown in Table 2.

Table 2. Final raw mixes, wt. %

Materials	Raw Mix I	Raw Mix II
Cement plant raw materials	73	74
CKD 1	14	12
Prep-waste 3	7	0
Prep-waste 2	6	0
Prep-waste 1	0	14

The compositions of these mixes with respect to the target mix and the calculated values of Bogue compounds are shown in Table 3a,b.

Table 3a. Composition of final raw mixes, wt. %

Analyte	Target Mix	Raw Mix I	Raw Mix II
SiO_2	13.86	12.86	13.39
Al_2O_3	3.13	3.01	3.09
Fe_2O_3	2.53	2.61	2.43
CaO	41.36	40.51	40.93
MgO	2.31	2.21	2.18
SO_3	0.49	3.27	2.74
Na_2O	0.09	0.12	0.10
K_2O	0.96	1.06	1.03
LOI	35.15	34.46	34.28

Table 3b. Bogue composition of clinkers from final raw mixes, wt. %

| Analyte	Target Mix	Raw Mix I	Raw Mix II
C_3S	57	52	50
C_2S	18	17	21
C_3A	6	5	6
C_4AF	12	12	12

CLINKER PRODUCTION AND CHARACTERIZATION

The raw mixes were pelletized and fired at $1400^{\circ}C$ for 50 min. to ensure complete clinkering. The firing at $1400^{\circ}C$ as compared to $1450^{\circ}C$ usually required for commercial clinker production was due to the presence of supplementary fuel from the prep-waste incorporated to the raw mix. The criterion for complete clinkering was less than 1.5% free lime content by mass in the resulting clinker. Periodic checks of the free lime in the clinkers using X-ray diffraction (XRD) was done to ensure complete burning. The final test clinkers were analyzed by XRF for oxide and Bogue composition; XRD was used for phase identification, and microscopical examination was done to study the phase distribution.

In XRD patterns (Figures 3 and 4) peaks at 32.2, 32.6, and 34.4 degrees correspond to C_3S and C_2S phases, whereas free lime, if present, will have a peak at 37.4 degrees.
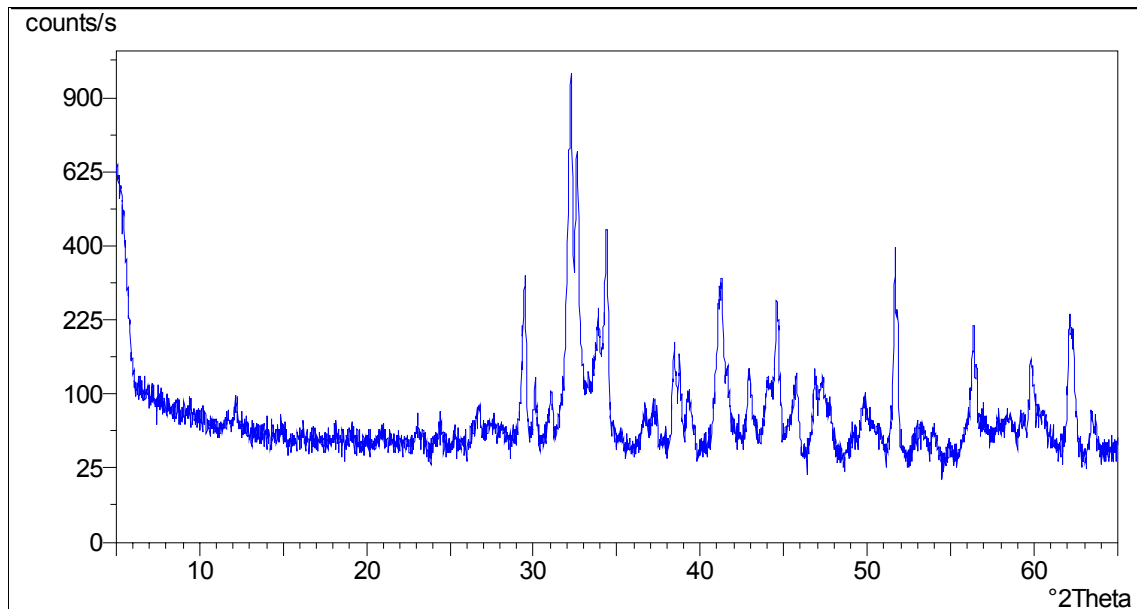
**Figure 3. XRD pattern of Mix I clinker showing peaks of major phases**
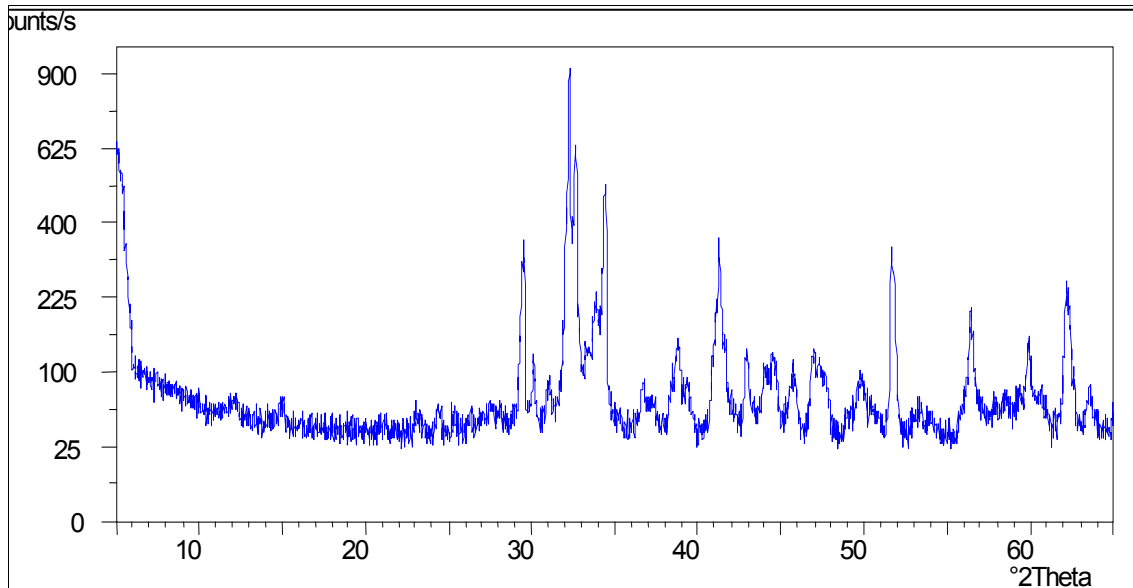
Figure 4. XRD pattern of Mix II clinker showing peaks of major phases

The XRD patterns for both clinkers show appropriate distribution of major clinker phases and only traces of free lime content. Similarly, the oxide analyses and the computed Bogue compounds of these clinkers, as shown in Table 4, appear reasonable. The levels of sulfates suggests that grinding without the addition of gypsum, and then blending with 50% ordinary portland would result in a composition close to that of a Type I/II cement.

Table 4. Chemical composition and Bogue analyses of clinkers, wt. %

Analyte	Raw Mix I	Raw Mix II
SiO_2	20.61	20.72
Al_2O_3	4.36	4.76
Fe_2O_3	3.56	3.72
CaO	64.42	63.93
MgO	3.48	3.39
SO_3	2.38	2.37
Na_2O	0.12	0.12
K_2O	1.03	1.09
LOI	0.00	0.00
Bogue compounds		
C_3S	64	59
C_2S	10	15
C_3A	6	6
C_4AF	11	11

Optical microscopy of the clinkers examined the formation and relative distributions of the major phases. The micrographs shown in Figures 5 and 6 suggest reasonable distribution of the major clinker phases.
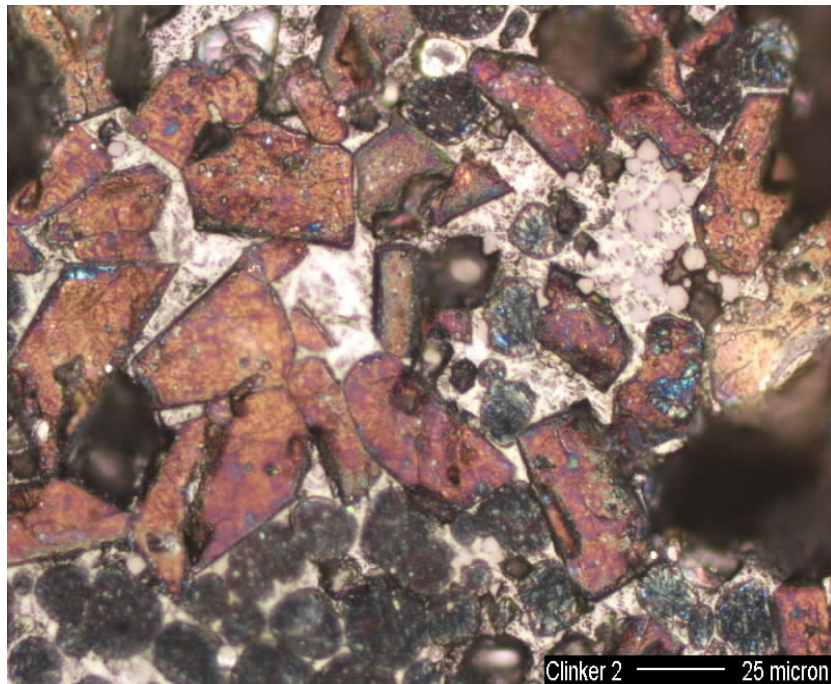
Figure 5. Mix I clinker showing formation and distribution of major phases
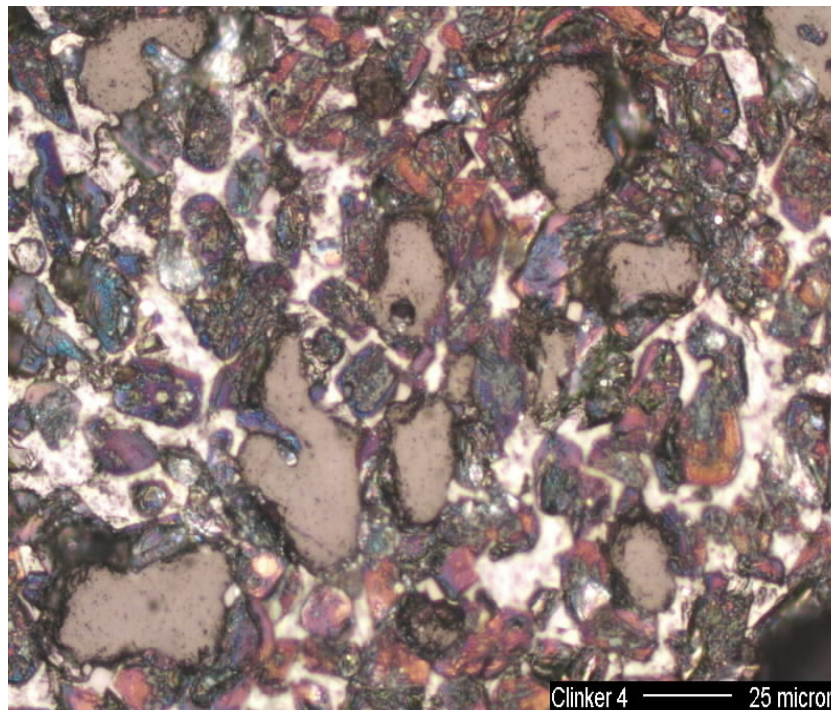
Figure 6. Mix II clinker showing formation and distribution of major phases

The large angular crystals in the micrographs (Figures 5 and 6) are alites (C_3S), and the round crystals with lamellae are belites (C_2S). The interstices are composed of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) - also known as the melt phases. Large gray areas are pores; higher porosity can lead to better grindability of clinkers.

CEMENTS PRODUCTION, TESTING, AND EVALUATION

In order to produce cement, the clinkers were ground in a ball mill to a fineness of about 350 m^2/kg. No gypsum was added during grinding since the clinkers had sufficient sulfate content. The ground materials were blended with 50% Type I/II cement to produce cements for testing and evaluation. The cements were tested as per the ASTM C 150, "Standard Specification for Portland Cement." The test included both chemical and physical evaluation on oxide composition, compressive strength, air content, time of set (both initial and final), and early stiffening.

Chemical composition, along with the Bogue analysis of cements as determined by XRF are shown in Table 5; the standard limits for Type I/II cement are also given for comparison.

Table 5. Chemical composition and Bogue analyses of cements, wt. %

Analyte	Mix I cement	Mix II cement	Standard limits
SiO_2	20.43	20.24	20 (min)
Al_2O_3	4.48	4.56	6 (max)
Fe_2O_3	3.59	3.59	6 (max)
CaO	60.83	61.67	N.A.
MgO	3.37	3.39	6 (max)
SO_3	4.19	3.62	3 (max)
Na_2O	0.15	0.15	N.A.
K_2O	1.58	1.57	N.A
LOI	1.08	0.98	3 (max)
Bogue compounds			
C_3S	45	51	N.A.
C_2S	24	19	N.A.
C_3A	6	6	N.A.
C_4AF	11	11	N.A.

The data on chemical composition indicate that cements meet the standard requirements for Type I/II cement except for the sulfur, which is marginally higher than the limit. This should not be an issue as many commercial cements are produced over-sulfated to enhance early strength properties. However, if desired, this can be conveniently corrected by blending with low sulfate cements.

The cements were evaluated for a series of physical tests in accordance with the ASTM C150 specification. The data are shown in Table 6 along with the standard requirements for each test for comparison.

Table 6. Data on ASTM C 150 tests on cements

	Mix I cement	Mix II cement	Requirements for Type I/II cement
ASTM C 204 - Fineness, air permeability (Blaine), m^2/kg			
	383	385	280 (min)
ASTM C 109 - Compressive strength, psi			
3-day	4100	3880	1740 (min)
7-day	4680	4580	2470 (min)
ASTM C 191 - Time of set, minutes			
Initial	110	110	45 (min)
Final	150	160	375 (max)
ASTM C 359 - False set penetration, mm (remix)			
	50	50	50
ASTM C 451 - Paste false set - early stiffening			
	88.9%	88.6%	50% (min)

It is apparent from the data that both cements conformed to all physical tests requirements of the ASTM C 150 specification. The cements exhibited normal setting and stiffening and strength properties. The compressive strength significantly exceeded the required minimum level. The early stiffening and early setting data were within the acceptable range for Type I/II cement. More over, the marginally high sulfate content in the test clinkers did not have any effect on the early setting and stiffening behavior of these cements. It may be pointed out that many commercial cements are purposely being produced over-sulfated for improved early strength, and the high 3-day strengths of the test cements verify that.

CONCLUDING REMARKS

By virtue of being rich in silica, alumina, and iron, coal prep-wastes can be used as a viable component of raw feed in cement production – as they can replace clay and shale in cement raw feed. Additionally, the presence of residual coal in the waste, can lead to fuel conservation.

High sulfur content in the prep-waste was made to react with the alkali-rich cement kiln dusts (CKDs) used in the raw mix as an additive. The alkalies reacted with sulfate in prep-waste and "locked" them as a calcium langbeinite compound in clinker. Calcium langbeinite compound imparts the same set regulating effect as gypsum in ordinary cement - therefore not requiring any additional gypsum during finish cement grinding.

The marginally high sulfates in the test clinkers should not be an issue as many commercial cements are being produced over-sulfated to enhance early strength properties. However, if desired, sulfate levels can be reduced by 1) adjusting the blending proportions with ordinary portland cements, 2) blending with cements of low sulfate levels, and 3) reducing the dosage of prep-waste.

The concept of converting coal prep-wastes (in conjunction with CKD) to cement can effectively address the issues of waste management and the interrelated environmental stresses faced by the coal mines and cement plants alike.

ACKNOWLEDGEMENTS

REFERENCES

[1] Fridman, I.A., Bikbau, M.Ya, Kaushanski, V.B., Barbaskev, G.K., "Use of Coal Beneficiation and Petrochemical Wastes in Cement Manufacture," Tsement, 1989 (12), pp 2-4.

[2] Vusipov, N. Kh., "Characteristics of Raw Mixes Containing Coal Beneficiation Wastes," Tsement, 1989 (12), pp 8-10.

[3] Kraplya, A.F., Upolovnikov, A.B., Tsvang, A.S., Mckin, P.I.,Sheiko, A.N., "Use of Coal Beneficiation Wastes and Improvement of Quality of Clinker," Tsement, 1989 (12), pp 12-13.

[4] Kuznetsova, T.V, Tandiiova, K.B., Kavsadza, T.E, Bihilashvili, B.V., Pievako, B.I., "Coal Beneficiation Wastes in Cement Manufacture," Tsement, 1989 (12), pp 15-16.

[5] Bhatty, J.I., "Portland Cement Production Using Mineral Wastes," Cement and Concrete Research," 1985, Vol. 15, pp 501-10.

[6] Bhatty, J. I., Gajda, J., and Miller, F. M., "Converting Illinois Coal Prep Wastes into Supplementary Portalnd Cements," Report 01-1/3.D-2, ICCI, Carterville IL, 2002.

[7] Bhatty, J. I., Gajda, J., and Miller, F. M., Use of high Carbon Fly Ash in Cement Manufacture, Cement Americas, pp. 32-34, May/June, 2001.