

FINAL TECHNICAL REPORT  
November 1, 2001, through October 31, 2002

Project Title: **CONVERTING ILLINOIS COAL PREP WASTES INTO  
SUPPLEMENTARY PORTLAND CEMENTS**

ICCI Project Number: 01-1/3.1D-2  
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ABSTRACT

This study entails the feasibility of utilizing Illinois coal prep waste in the manufacture of cement. Coal prep wastes from Illinois coal mines were used together with cement kiln dust (CKD), as a component of raw feed in producing portland cement. The use of prep waste was maximized as a source of silica, alumina, and iron content of the raw feed. Sulfur in the waste was caused to react with alkalis in CKD to produce clinker with sulfate content somewhat higher than that of normally produced clinkers. The residual coal in the prep waste served as a supplementary fuel during firing. The clinkers were ground and blended with regular cement to produce portland cements compliant with ASTM C-150 specification.

Several combinations of prep waste, CKD, and raw materials from different Illinois cement plants were tested in the laboratory to generate clinkers. From these results, a combination of prep wastes from Turriss and Monterey mines with raw materials and CKD from Dixon-Marquette appeared most promising. Up to 14% each of prep waste and CKD was combined with raw material from Dixon-Marquette to produce two batches of clinker. The clinkers were produced by firing the raw mixes at 1400°C as compared to 1450°C usually required for commercial clinker production.

Microscopical examination of the clinkers confirmed the presence and distribution of the major phases typical of a normal clinker. The clinkers were ground to a fineness of 350 m<sup>2</sup>/kg Blaine and blended with ordinary cement to produce test cements for evaluation. The clinkers did not require addition of gypsum because the sulfates in them were most likely present as calcium langbeinite, which is a soluble sulfate compound that can control setting properties similar to gypsum in normal portland cement.

These cements showed chemical and physical properties comparable with those of commercial products when tested for compliance with the ASTM C-150 specification.

## EXECUTIVE SUMMARY

The objective of this project was to convert Illinois coal prep wastes, together with CKD, into portland cement by using them as components of cement raw feed. Since the prep wastes are rich in silica, alumina, and iron content, they were used in replacing shale, clay, and mill-scale in the formulation of cement raw feed. The presence of a high carbon content (about 25%) in the prep wastes was responsible for providing a significant saving in purchased fuel requirements during the clinker firing. Finally, sulfur in the prep wastes was captured with lime (provided by limestone) and alkalis (from CKD) and retained in the clinker.

Several prep waste samples were collected from mining operations in Illinois, and a bench-scale parametric study on the formulation of raw mixes was carried out. Clinkers were made from these raw mixes and evaluated. The use of prep waste was optimized to achieve maximum material and fuel benefits. Based on data from the tests on materials used and the resulting clinkers, two of the best combinations were selected for bulk clinker production and evaluation. These were:

- Turris Mine/Randolph Mine prep wastes – CKD and raw materials from Dixon Marquette Cement plant
- Monterey Mine prep waste – CKD and raw materials from Dixon Marquette Cement plant

For each combination, up to 14% prep waste and 14% CKD were used as components in the raw mix (replacing up to 28% of the traditional raw feed by mass). This resulted in the substitution of 80 to 100% of the clay, 25 to 75% of the sand, and 100% mill-scale in the respective cement raw mixes. The average loss on ignition (LOI) of the prep wastes was about 25%, giving an average heat value of close to 3000 Btu/lb.

The results of the burnability tests also suggested that the required clinkering temperature of the raw mixes made with prep wastes and CKD was around 1400°C, which was noticeably lower than 1450°C usually required for normal clinkers. This may be attributed to: 1) the silica in the prep waste being especially reactive with lime, 2) the higher sulfate content in raw mix, that may contribute to higher clinker melt phase generation at lower temperatures, and 3) prep waste carbon contents providing intimate heat transfer by virtue of proximity.

Fifty-pound kiln feed batches were prepared using the respective prep wastes with CKD and raw materials by grinding, blending, and pelletizing - followed by firing to produce clinkers. The clinkers were characterized by XRD for their major phases ( $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ ), and free lime, to ensure complete burning. Most likely, the higher alkali-sulfate contents contained in the clinker were in the form of calcium langbeinite. This compound imparts the same control setting properties as gypsum in ordinary cement, therefore the clinker could be ground without gypsum and directly blended with ordinary portland cement to produce cements in compliance with ASTM C-150 specifications. Blending was at a dosage of 50% by mass.

The test data show that the cement produced from the prep waste-CKD combination complied with the ASTM C-150 specifications, except for the SO<sub>3</sub> level. Both cements had chemical and physical properties comparable to those of normal commercial cements.

The study has confirmed that the concept of using prep waste for cement production can lead to an efficient high-volume utilization of Illinois coal prep wastes.

This should impart several material, operational, energy, environmental, and economical benefits both to coal mines that generate prep wastes, and to the cement plants that would be willing to use them for production. Cement plants should also be able to recycle their high-alkali CKDs, a waste they otherwise must discard.

## OBJECTIVES

The objective of the project was to demonstrate the use of Illinois coal prep waste, in combination with cement kiln dust (CKD), for manufacturing portland cement by using it as a raw feed component as well as a fuel supplement. Being similar in chemical composition to shale and clay, the prep wastes could partially or fully substitute for shale, clay, and even the corrective materials such as mill-scale and sand as cement raw materials, which are otherwise mined or purchased. The residual coal in the prep waste would supplement fuel for the energy-intensive process of cement manufacturing. CKD in turn could provide alkalis to react with sulfur in the prep waste, and additionally, provide lime for the cement raw mix.

Based on preliminary calculations and approximations, the following objectives seem plausible:

- A 14% use of prep wastes in the kiln feed of the four cement plants in Illinois (combined capacity of 2.5 million tons/year), could consume 260,000 tons of waste each year to manufacture commercial cement. Likewise, a use of 14% CKD in the feed could lead to the removal of landfilled CKD and conserve limestone resources.
- Almost 200,000 tons per year of shale, clay, and iron ore would not have to be mined or purchased, conserving valuable raw material sources.
- Depending upon the energy recovery from the prep wastes, the cement plant using 15% prep wastes with 25% loss on ignition (LOI), should be able to realize about 4% energy saving.
- Being glassy or cryptocrystalline in nature, the inorganic residue of prep wastes should facilitate a reaction with lime at reduced clinkering temperature. This would permit increased kiln production and reduced energy consumption.
- This "waste-to-product" approach would generate a saleable product while significantly reducing wastes and related environmental stresses in Illinois.

Both the cement plants and the coal prep facilities should be able to realize the economic benefits of this concept. However, a large-scale demonstration would be prudent to further develop this technology for converting large volumes of prep waste into saleable cement.

## INTRODUCTION AND BACKGROUND

More than 5 million tons of prep wastes are generated from coal cleaning operations in the State of Illinois each year. These prep wastes are routinely disposed of in landfills. Years of accumulation of these wastes must presently amount to several hundred million tons. Except for occasional use as mining back fill, these wastes have not found a beneficial reuse. At the same time, cement plants in Illinois generate about 150,000 tons of cement kiln dust (CKD) each year. Although the bulk of the CKD is now being recycled, large amounts of typically alkali-rich CKD still remain accumulated in the old

landfills, where they can potentially leach into the ground and cause environmental and ecological imbalance.

Prep wastes typically consist of silica, alumina, iron oxide, lime, magnesia, sulfur, and residual carbon (from coal). Since this composition is similar to clay and shale used in cement manufacture, the prep wastes appear to be an appropriate substitute for reformulating 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 in the clinker. Residual carbon in the prep waste would contribute to fuel saving during the energy-intensive pyroprocessing of clinker.

It is anticipated that, by virtue of their reactive nature, the prep wastes would facilitate high lime combinability, and form clinker at a reduced temperature. This would lead to energy conservation and production enhancement. It is also anticipated that the sulfate formed in the clinker will be largely in the form of calcium langbeinite, which has a set regulating effect similar to gypsum in ordinary cement. This would preclude the need for addition of gypsum during finish grinding.

Therefore, this study reports on the use of coal prep waste in making portland cement. A series of mixes were formulated using prep wastes from local mines with CKD and raw materials from Illinois cement plants. Use of prep wastes and CKD was maximized in replacing shale, clay, sand, and mill-scale. Bulk clinkers were prepared from the two most promising raw mixes. The clinkers were ground and blended with ordinary cement to produce cement that conforms to ASTM C-150 specifications.

## EXPERIMENTAL PROCEDURES

The experimental investigations were conducted in two phases as follows:

### **Phase I - Bench Scale Studies**

Several samples of prep wastes were collected from Illinois coal-processing plants, including those in close proximity to the cement plants operating in Illinois. Likewise, samples of CKD and typical raw materials (limestone, shale, clay, sand, mill-scale, etc.) from cement plants were procured. Details on sources are as follows:

Coal Prep Wastes:	Rend Lake Monterey White County Randolph Turriss
Cement Raw Materials and CKD:	Illinois Cement Lone Star Dixon Marquette

Using X-ray fluorescence (XRF), the prep wastes, CKDs, and raw material samples were analyzed for their chemical composition. The prep wastes were subjected to

differential scanning calorimetry (DSC) to determine the heating value, and also the temperature of volatilization of any combustible organics.

Based on compositional compatibility, prep waste with LOI around 25% and CKDs rich in alkali were selected for raw mix formulations. Several cement raw mixes were made using the selected combinations. 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. If necessary, minor amounts of corrective materials such as shale, clay, and sand were added to the raw mix to adjust the lime saturation factor, silica modulus, and other burnability factors.

Each mixture was pelletized and fired in a muffle furnace at temperatures sufficient to cause clinkering. As is indicated later, depending upon the composition of raw mixes, clinkers were prepared at three temperatures of 1350°C, 1400°C, and 1450°C. For the final raw mixes, the temperature was 1400°C and residence time of 50 minutes. The clinkers were tested for abundance and distribution of major phases by XRF, microscopical, and XRD analyses.

### **Phase II - Pilot Scale Studies**

Based on mix composition and firing conditions tested above, the two best raw mix formulations were selected for bulk clinker production. Due to the abundance and compositional uniformity of CKD discarded from Dixon Marquette Cement plant, this material was the chosen CKD, and prep waste from Turris, Monterey, and Randolph mines were selected for this phase of the study. Two large batches of raw mix were prepared to be as similar in composition to the cement plant kiln feed as permitted by practical constraints.

Each kiln feed was pelletized and fired at 1400°C to produce sufficient clinker for the required testing and evaluation. The clinkers were analyzed by XRF for oxide and Bogue composition; XRD was used for phase identification, and microscopical examination was carried out to study the clinker phase distribution. The XRD analyses suggested that sulfates in the clinker were most likely present as calcium langbeinite,\* which can regulate setting behavior in the same way as gypsum in ordinary cement. The experimental clinker was therefore ground fine without gypsum and blended with 50% ordinary portland cement made available by Dixon Marquette. The cements were evaluated for compliance with ASTM C-150 specifications for compressive strength, time of set, soundness, and other performance related properties.

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\* The XRD evidence for calcium langbeinite is equivocal. On the other hand, there is no evidence of other sulfate phases. As calcium langbeinite is often poorly crystalline, we still believe it is present as the principal sulfate-containing phase in the clinkers.

## RESULTS AND DISCUSSION

### Phase I - Bench Scale Studies

#### Task 1. Procurement of Samples

The coal prep wastes were collected from five coal-processing facilities identified as Rend Lake, Monterey, White County, Randolph, and Turriss mines. They were dried, ground, and sampled for analysis. Similarly, samples of raw materials, companion kiln feeds, and CKDs from three Illinois cement plants - Illinois Cement Company, Lone Star, and Dixon-Marquette, were acquired and analyzed.

#### Task 2. Material Characterization

The prep wastes, CKDs, and the cement raw materials were analyzed using X-ray fluorescence spectroscopy (XRF) for content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, SO<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and loss on ignition (LOI).<sup>\*</sup> Typical data on select prep wastes and CKD are shown below in Table 1.

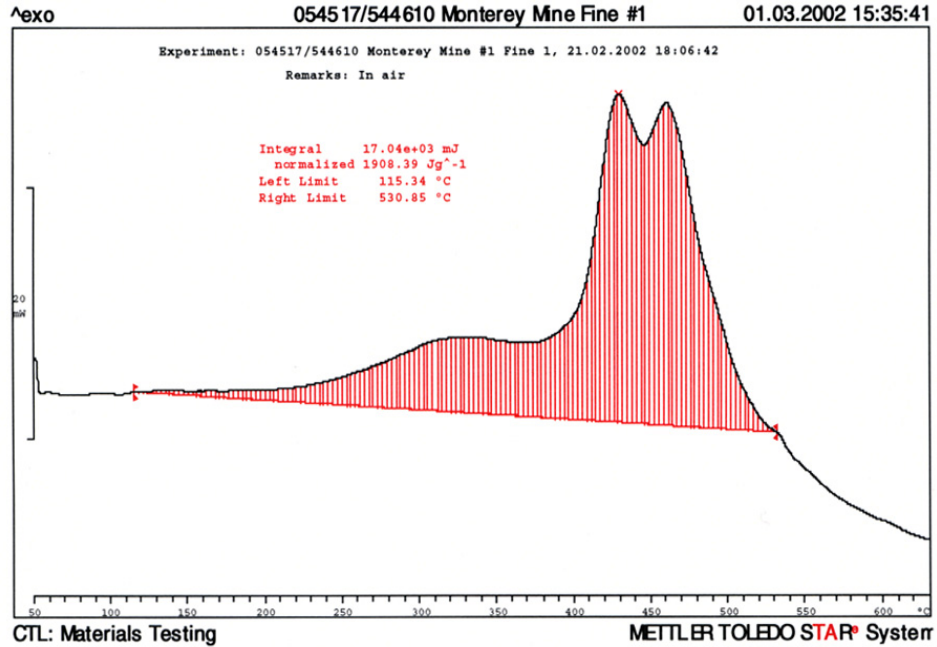
**Table 1. Composition of mine prep wastes and cement plant CKDs, wt. %**

Analyte	Monterey	Randolph	Turriss	Rend Lake	White County	Dixon Marquette CKD	Illinois Cement CKD	Lone Star CKD
SiO <sub>2</sub>	27.38	21.28	43.24	46.33	13.03	10.77	17.41	15.83
Al <sub>2</sub> O <sub>3</sub>	9.82	5.69	11.17	13.76	4.24	2.92	6.65	4.56
Fe <sub>2</sub> O <sub>3</sub>	12.63	15.78	9.6	3.79	3.11	1.46	2.15	1.77
CaO	17.0	12.32	3.8	0.63	2.63	33.42	39.22	42.84
MgO	0.67	0.04	1.13	1.06	0.39	1.87	1.78	1.47
SO <sub>3</sub>	5.26	15.07	3.25	0.32	0.96	8.01	1.15	11.21
Na <sub>2</sub> O	0.4	0.22	0.74	2.29	0.35	0.22	0.38	0.57
K <sub>2</sub> O	1.18	0.76	2.04	0.73	0.83	9.89	1.06	4.31
LOI	24.5	26.63	23.94	30.27	74.53	27.98	29.72	15.21

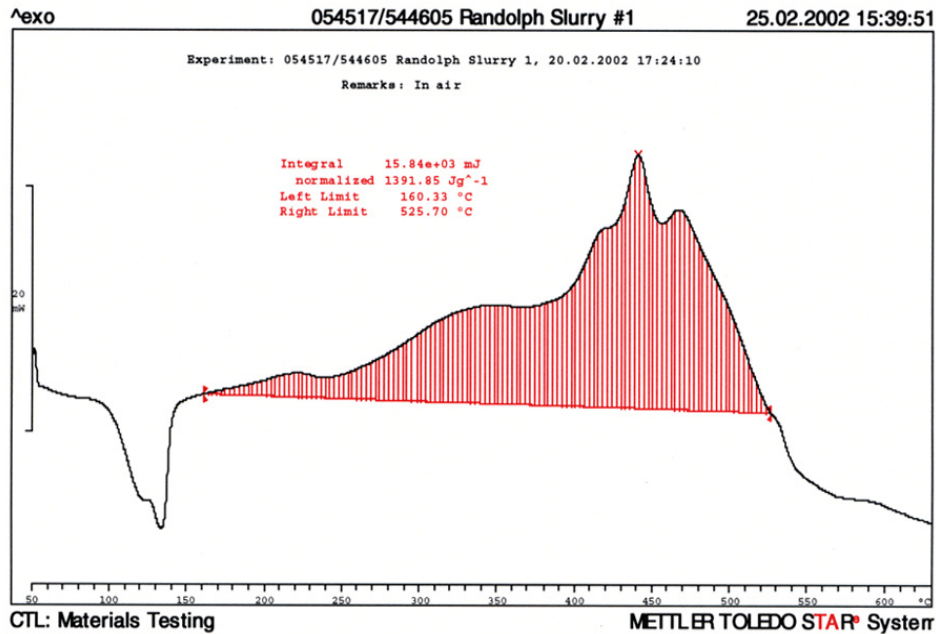
The data indicate that in general the prep wastes were rich in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO, confirming their appropriateness for use as clay/shale substitutes in cement raw feed. They also contain significant amounts of sulfur (shown as SO<sub>3</sub>). The LOI values for most prep wastes were around 25% except for Rend Lake and White County wastes that have higher LOIs, indicating a potential for excessive heat during the early part of raw feed processing in cement kiln systems. CKDs are typically rich in CaO and alkalis. Alkalis are 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 evaluate the heat content and characteristics of the volatile organic matter present. Selected DSC plots are shown in Figs. 1 and 2.

<sup>\*</sup> LOI is also an indication of the carbon content in prep wastes.



**Fig. 1 DSC plot showing exothermic peaks for Monterey prep waste**



**Fig. 2 DSC plots showing exothermic peak Randolph prep waste**

Large exothermic peaks starting around 350°C indicate a heat release by combustion of hydrocarbons from residual coal in the prep wastes. However small peaks at lower temperatures are indicative of the presence of volatile and combustible components in the wastes. This latter material may be released at temperatures so low that it may escape combustion in the cement kiln as unburned volatile organic compounds (VOC's) and cause emission problems.



The raw materials and kiln feeds from the three plants were analyzed for major oxides by XRF for use in mix design formulations and bench scale burns. Typical data for Dixon Marquette raw materials and its kiln feed are shown in Table 2.

**Table 2. Analyses of Dixon Marquette Cement raw materials and kiln feed, wt. %**

Analyte	Kiln feed	Limestone	Clay	Sand	Mill-scale
SiO <sub>2</sub>	12.48	6.83	39.74	81.83	3.58
Al <sub>2</sub> O <sub>3</sub>	2.84	1.51	13.81	3.56	0.07
Fe <sub>2</sub> O <sub>3</sub>	2.25	0.53	3.43	3.33	99.65
CaO	42.54	47.5	18.12	3.2	1.37
MgO	2.44	2.56	1.45	0.64	0.04
SO <sub>3</sub>	0.67	0.36	1.47	0.13	0.05
Na <sub>2</sub> O	0.04	0.04	0.18	0.50	0.21
K <sub>2</sub> O	1.09	0.80	2.2	0.86	0.08
LOI	35.81	39.92	18.96	6.00	-6.73

**Tasks 3, 4, and 5. Raw Feed Formulation, Clinker Production, and Burnability Study**

The chemical composition of the raw materials, prep wastes, CKD, and the kiln feeds acquired from cement plants were examined for the potential to be used in raw mixes for producing clinkers of acceptable quality.

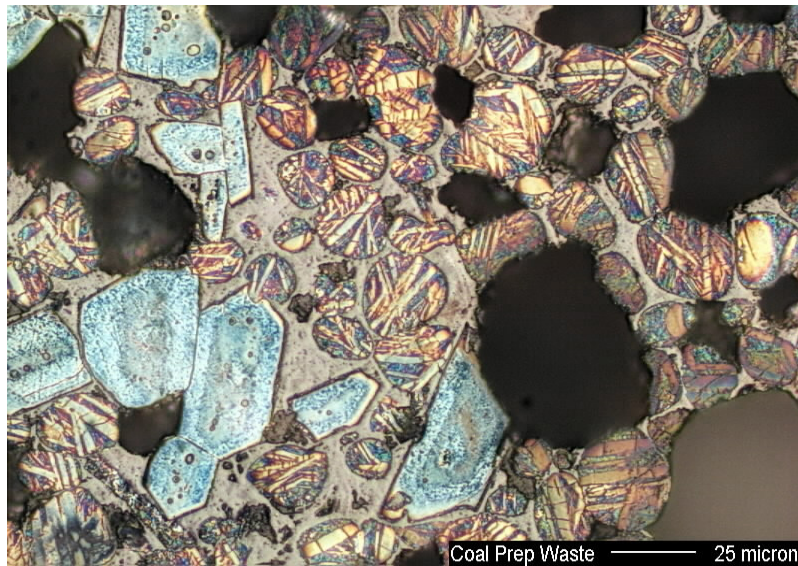
Rend Lake and White County wastes were not considered for further testing because of their high volatile organic contents, which, as mentioned earlier, can cause excessive premature heating in the temperature range of preheater towers, or in the chain sections of long kilns. Dixon Marquette was preferred because of the composition of their CKD and the potential for a large-scale demonstration at their plant. The higher alkali contents of their CKD (as compared to Illinois Cement CKD) were beneficial in “tying up” more sulfur in prep wastes.

Based on compositional compatibility, four raw mix formulations were made using Randolph and Monterey wastes with CKDs and raw materials from Dixon Marquette and Lone Star to develop clinker of the desired composition; the formulations are shown in Table 3. The mixes were prepared by intergrinding the ingredients in the required proportions. The materials were pelletized and fired in the muffle furnace at 1450°C for one hour to insure complete clinkering.

**Table 3. Mix formulations using raw materials, coal prep wastes, and CKDs, wt. %**

Dixon Marquette	Mix I	Mix II	Lone Star	Mix III	Mix IV
High limestone	35	34	High Limestone	39	43
Medium limestone	33.5	33.5	Low Limestone	45	41
Clay	-	3	LKD	3	3
Sand	-	1.5	Slag	-	-
Mill-scale	-	-	-	-	-
CKD	12	13	CKD	8	8
Monterey prep waste	-	13	Monterey Prep Waste	-	5
Randolph prep waste	19.5	-	Randolph Prep Waste	5	-

XRF analyses indicated a lack of  $C_3S$  and abundance of  $C_2S$  phase in the clinkers produced. A microscopical examination of the polished section confirmed these phase distribution (see Fig. 3).



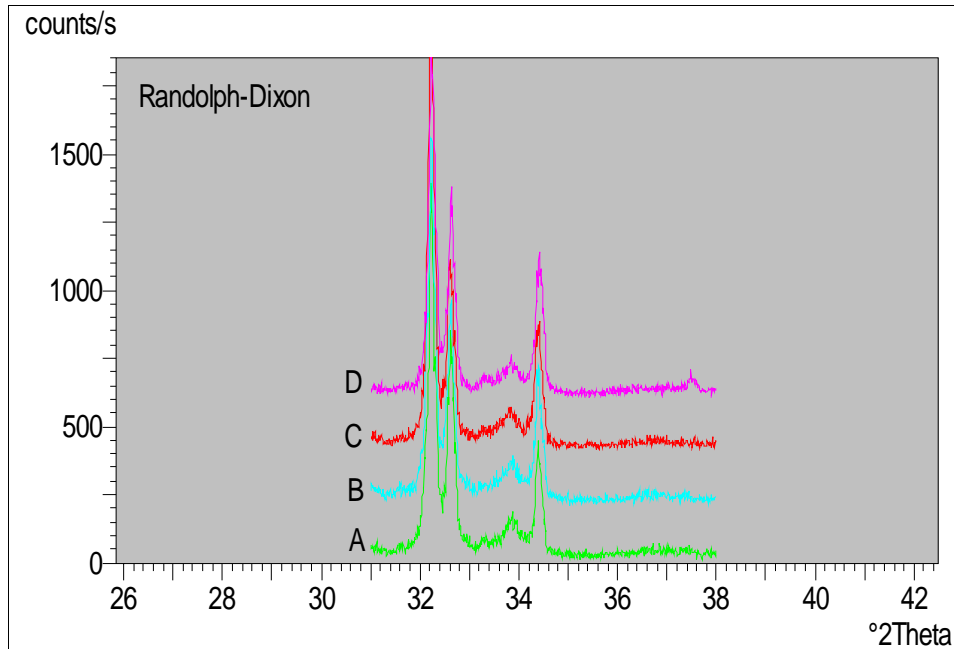
**Fig. 3 Prep waste clinker showing lack of  $C_3S$  (angular crystals) and abundance of  $C_2S$  (rounded crystals), gray interstitial is the melt phase that contains  $C_3A$  and  $C_4AF$ ; dark random spots are pores**

The mix designs were reformulated to adjust the relative amounts of  $C_3S$  and  $C_2S$  phases in the final clinker by enhancing with limestone as “sweetener.”

Since the composition of raw material from Dixon Marquette Cement allowed the maximum use of prep wastes, it was decided to focus on the mixes using Dixon Marquette raw materials.

For each of the target mix designs, three additional variations were prepared with incremental levels of limestone as “sweetener” to enhance the  $C_3S$ . This resulted in a total of eight clinkers. Clinkers were made at  $1350^{\circ}C$  to avoid overburning and to provide a practical preliminary estimate of potential energy conservation.

X-ray diffraction (XRD) analyses indicated that addition of the sweetener increased the  $C_3S$  phase concentration up to a limit. Beyond that, the free lime concentration increased. The effects were more pronounced with Randolph-Dixon clinkers, as illustrated by clinker D in Fig. 4; XRD plots of other clinkers are also shown for comparison.



**Fig. 4 Clinker D shows free lime peak at 37.4 degrees; all clinkers show increasing  $C_3S$  and  $C_2S$  phases with increased sweetener; clinkers A, B, C, and D are with increasing addition of sweetener**

In Fig. 4,  $C_3S$  and  $C_2S$  phases are indicated by peaks at 32.2, 32.7, and 34.4 degrees. A peak at 37.4 degrees indicates the presence of free lime. XRF analyses and Bogue composition confirmed the major phase concentrations in the clinkers.

Based on the XRD data and the indication of some free lime, the next test batches were scheduled for preparation and firing at 1400°C. At this point, prep waste from Turriss Mine in Elkhart, IL was included for testing and evaluation. Being close to most of the cement plants in northern Illinois including Dixon-Marquette, Turriss is a promising source for prep waste in cement manufacturing for economic reasons. CKD from the Dixon Marquette discard pile was also included in the studies. Relative abundance and uniformity of composition of this CKD (as compared to previous sample taken from the baghouse) prompted this consideration; the CKD composition is shown in Table 4.

**Table 4 Composition of CKD from Dixon Marquette discard pile, wt. %**

Analyte	CKD
SiO <sub>2</sub>	12.61
Al <sub>2</sub> O <sub>3</sub>	3.41
Fe <sub>2</sub> O <sub>3</sub>	1.41
CaO	41.74
MgO	1.98
SO <sub>3</sub>	1.96
Na <sub>2</sub> O	0.13
K <sub>2</sub> O	1.75
LOI	35.81

Composition of Turriss prep waste is already given in Table 1. Turriss prep waste is richer in SiO<sub>2</sub> and contains less sulfur but has LOI similar to the Randolph and Monterey prep wastes. Turriss prep waste was used in combination with Randolph to adjust the sulfur content. The material combinations of the final two mixes designated as Raw Mix 2 and Raw Mix 4 are shown in Table 5.

**Table 5. Final raw mixes, wt. %**

<b>Materials</b>	<b>Raw Mix 2</b>	<b>Raw Mix 4</b>
Dixon Marquette raw materials	73	74
Dixon Marquette CKD	14	12
Turriss prep waste	7	0
Randolph prep waste	6	0
Monterey prep waste	0	14

Again, the use of prep waste was maximized. The raw mixes were fired at 1400°C to ensure complete reaction. The XRD tests on the resulting clinkers suggested reasonable conversion to major clinker phases, with only traces of free lime present.

## **Phase II- Pilot-Scale Studies**

### Task 6. Raw Mix Preparation and Burns

Two raw mix formulations (Raw Mix 2 and Raw Mix 4) as finalized from Task 5 tests were used for preparation of kiln feeds for pilot scale clinker production. Details of material proportions along with the actual kiln feed from Dixon Marquette (shown as “Target Mix”) are given in Table 6.

**Table 6. Final raw mix formulations and target mix from Dixon Marquette, wt. %**

<b>Materials</b>	<b>Target Mix</b>	<b>Raw Mix 2</b>	<b>Raw Mix 4</b>
Dixon limestone	82.5	69.5	70
Clay	11.0	1.5	0
Sand	4.0	1	3
Mill-scale	1.5	0	0
CKD	0	14	12
Corrective material	1	1	1
Turriss prep waste	0	7	0
Randolph prep waste	0	6	0
Monterey prep waste	0	0	14

The compositions of these mixes with respect to the target mix along with the calculated Bogue analyses of major clinker phases is shown in Table 7 for comparison.

Fifty-pound raw mix batches were prepared by using raw materials from Dixon-Marquette plant in the proportions given above by crushing and intergrinding the ingredients so that approximately 80% of the material passed a 200-mesh (75 µm) sieve. These raw mixes were then pelletized and dried before introduction into the furnace for firing.

**Table 7. Composition of final raw mixes, wt. %**

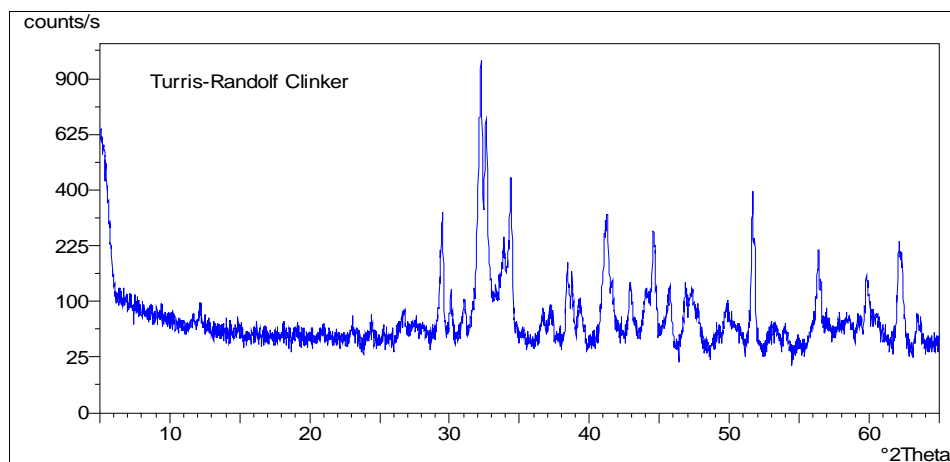
Analyte	Target Mix	Raw Mix 2	Raw Mix 4
SiO <sub>2</sub>	13.86	12.86	13.39
Al <sub>2</sub> O <sub>3</sub>	3.13	3.01	3.09
Fe <sub>2</sub> O <sub>3</sub>	2.53	2.61	2.43
CaO	41.36	40.51	40.93
MgO	2.31	2.21	2.18
SO <sub>3</sub>	0.49	3.27	2.74
Na <sub>2</sub> O	0.09	0.12	0.10
K <sub>2</sub> O	0.96	1.06	1.03
LOI	35.15	34.46	34.28
Bogue compounds			
C <sub>3</sub> S	57	52	50
C <sub>2</sub> S	18	17	21
C <sub>3</sub> A	6	5	6
C <sub>4</sub> AF	12	12	12

The raw mix was fired at 1400°C. The criterion for completeness of burning was the production of clinker with less than 1.5% free lime by mass. Periodic checks of the free lime content of the clinker using X-ray diffraction was done to ensure completeness of burning. Approximately 10 lbs of each clinker was produced for subsequent evaluation.

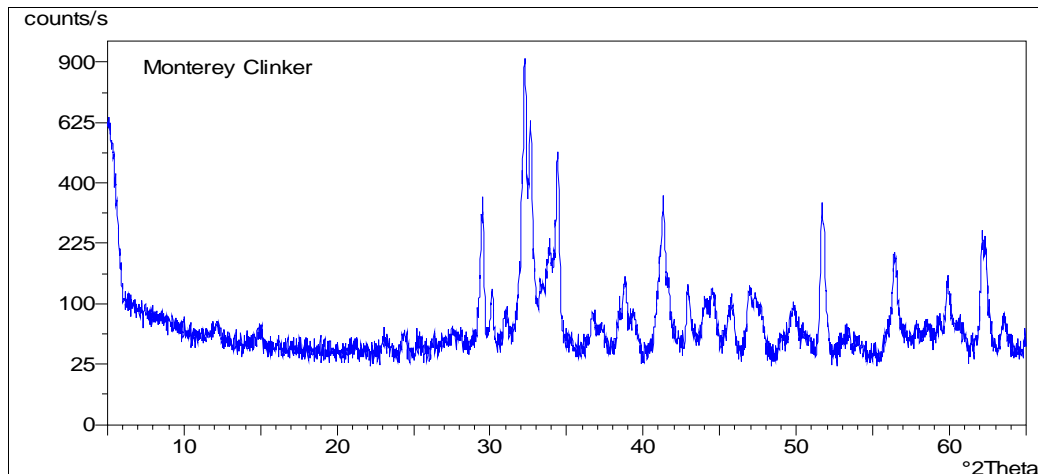
#### Task 7. Characterization and Evaluation of Clinkers

The clinkers produced in Task 6 were characterized for their physical and chemical properties using the following qualitative and quantitative tests.

X-Ray Diffraction: X-ray diffraction (XRD) was used to identify crystalline phases present in clinker such as alite (C<sub>3</sub>S), belite (C<sub>2</sub>S), tricalcium aluminate (C<sub>3</sub>A), and tetracalcium aluminoferrite (C<sub>4</sub>AF), along with the free lime (CaO) and free periclase (MgO) as shown in Figs. 5 and 6. Peaks at 32.2, 32.6, and 34.4 degrees correspond to C<sub>3</sub>S and C<sub>2</sub>S phases, whereas free lime would appear at 37.4 degrees.



**Fig. 5 XRD pattern of Mix 2 clinker showing peaks of major phases**



**Fig. 6 XRD pattern of Mix 4 clinker showing peaks of major phases**

As can be seen from the XRD patterns, both clinkers show appropriate distribution of major clinker phases and only traces of free lime content.

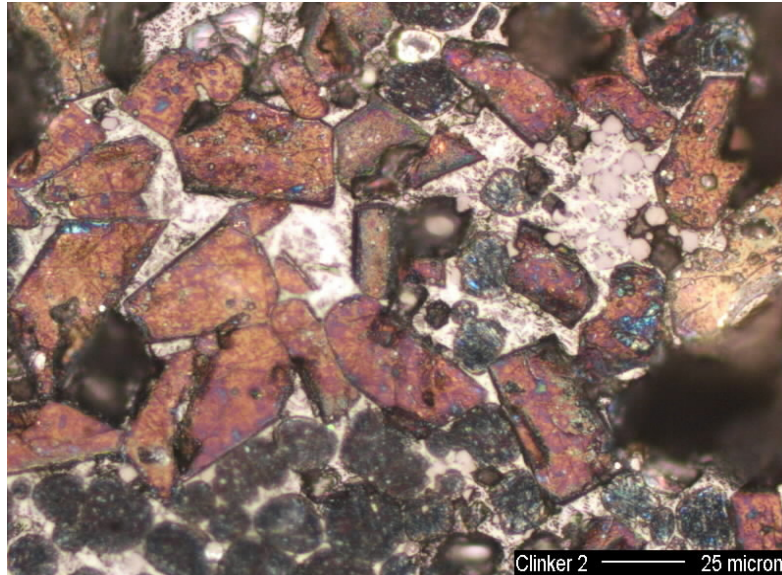
X-Ray Fluorescence: The oxide analysis by XRF and the computed Bogue compounds are shown in Table 8.

**Table 8. Chemical composition and Bogue analyses of final clinkers, wt. %**

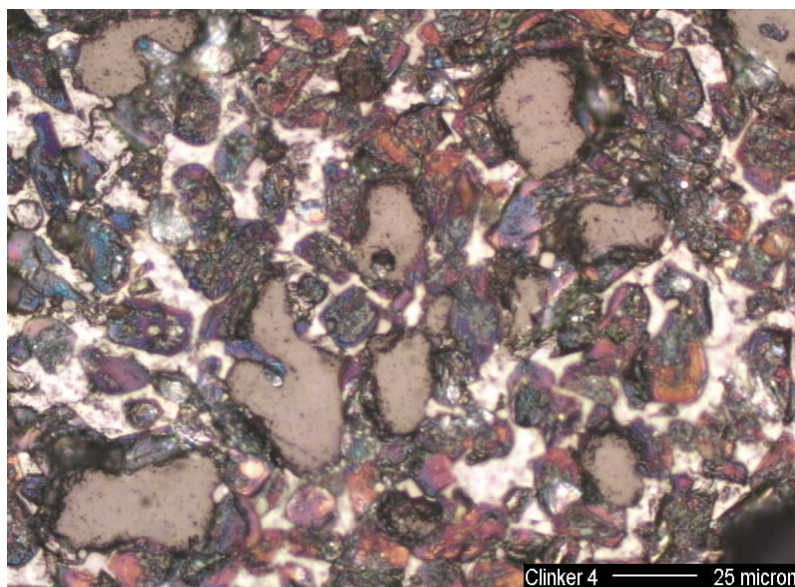
Analyte	Raw Mix 2	Raw Mix 4
SiO <sub>2</sub>	20.61	20.72
Al <sub>2</sub> O <sub>3</sub>	4.36	4.76
Fe <sub>2</sub> O <sub>3</sub>	3.56	3.72
CaO	64.42	63.93
MgO	3.48	3.39
SO <sub>3</sub>	2.38	2.37
Na <sub>2</sub> O	0.12	0.12
K <sub>2</sub> O	1.03	1.09
LOI	0.00	0.00
<b>Bogue compounds</b>		
C <sub>3</sub> S	64	59
C <sub>2</sub> S	10	15
C <sub>3</sub> A	6	6
C <sub>4</sub> AF	11	11

The chemical composition and the computed Bogue phase contents in the clinkers appear reasonable. The levels of sulfates suggests that grinding without the addition of gypsum, and then blending with 50% ordinary portland will result in a composition close to that of a Type I/II cement.

Optical Microscopy: Polished sections of the clinkers were examined by reflected light microscopy to determine the relative quantities and distributions of the major phases. The micrographs shown in Figs. 7 and 8 suggest reasonable distribution of the major phases.



**Fig. 7 Mix 2 clinker showing formation and distribution of major phases, large angular crystals in the micrographs are alites, the round crystals with lamellae are belites; the interstices are composed of tricalcium aluminate and tetracalcium aluminoferrite - also known as the melt phases. Large gray areas are pores. Higher porosity can lead to better grindability of clinkers.**



**Fig. 8 Mix 4 clinkers showing formation and distribution of major phases**

### Task 8. Production of Cements

The clinkers were ground in a ball mill to a fineness of about 350 m<sup>2</sup>/kg. Since the clinkers had sufficient sulfate content, no gypsum was added. The ground clinker was blended with 50% Type I/II cement from Dixon-Marquette to produce final cements for testing and evaluation.

### Task 9. Testing of Cements

The cements were tested for compliance with ASTM C-150, "Standard Specification for Portland Cement." The test regimen includes both chemical and physical tests on compressive strength, air content, time of set (both initial and final), and early stiffening.

Chemical compositions and Bogue analyses of the blended cements as determined by XRF are shown in Table 9. The standard requirements for Type I/II cement are also given for comparison.

**Table 9. Chemical composition and Bogue analyses of cements, wt. %**

<b>Analyte</b>	<b>Raw Mix 2 cement</b>	<b>Raw Mix 4 cement</b>	<b>Standard requirements</b>
SiO <sub>2</sub>	20.43	20.24	20 (min)
Al <sub>2</sub> O <sub>3</sub>	4.48	4.56	6 (max)
Fe <sub>2</sub> O <sub>3</sub>	3.59	3.59	6 (max)
CaO	60.83	61.67	N.A.
MgO	3.37	3.39	6 (max)
SO <sub>3</sub>	4.19	3.62	3 (max)
Na <sub>2</sub> O	0.15	0.15	N.A.
K <sub>2</sub> O	1.58	1.57	N.A.
LOI	1.08	0.98	3 (max)
<b>Bogue compounds</b>			
C <sub>3</sub> S	45	51	N.A.
C <sub>2</sub> S	24	19	N.A.
C <sub>3</sub> A	6	6	N.A.
C <sub>4</sub> AF	11	11	N.A.

Chemical data indicates that cement meets the standard requirements for a Type I/II cement except for the sulfur, which is marginally higher than the limit; this can be conveniently corrected by blending with low sulfate cements.

The cements were subject to a series of physical tests as require by the ASTM C150 specification. They included compressive strength, air content, time of set (both initial and final), and early stiffening. Tests data are shown in Table 10; standard requirements for each test are also given for comparison.



**Table 10. Data on ASTM C-150 tests on cements**

	<b>Mix 2 cement</b>	<b>Mix 4 cement</b>	<b>Requirement for Type I/II cement</b>
<b>ASTM C 204 - Fineness, air permeability (Blaine), m<sup>2</sup>/kg</b>			
	383	385	280 (min)
<b>ASTM C 109 - Compressive strength, psi</b>			
3-day	4100	3880	1740 (min)
7-day	4680	4580	2470 (min)
<b>ASTM C 191 - Time of set, minutes</b>			
Initial	110	110	45 (min)
Final	150	160	375 (max)
<b>ASTM C 359 - False set penetration, mm (remix)</b>			
	50	50	50
<b>ASTM C 451 - Paste false set - early stiffening</b>			
	88.9%	88.6%	50% (min)

The data show that both cements conform to all physical tests requirements of the ASTM C-150 specification for Portland cements. The cements show normal setting and strength development characteristics. Both the early stiffening and early setting data are within the acceptable range for a Type I/II cement. The compressive strength significantly exceeds the required minimum level. It also appears that the marginally high sulfate did not have any effect on the early setting and stiffening behavior of these cements. Many commercial cements are purposely being prepared over-sulfated for early strength gains, and the high 3-day strength of the tested cements verify that trend.

### CONCLUSIONS AND RECOMMENDATIONS

Coal prep wastes appear to be a viable component of raw feed in cement production. By virtue of being rich in silica, alumina, and iron, they can be used in place of clay and shale in cement raw feed.

The study demonstrated that up to 14% each of prep waste and CKD could be used as a substitute in the raw feed (replacing up to 28%). This resulted on average in the substitution of 90% of the clay, 50% of the sand, and 100% of the mill-scale in cement raw mixes. This could translate to the conservation of natural clay and shale resources and eliminate the use of mill-scale and sand that are otherwise purchased.

Clinkers were made at noticeably lower temperatures than normally used in making clinker, without affecting the extent of clinkering of the raw mix. This can lead to the conservation of fuel as well as an increase in clinker production.

Cements produced from the raw mixes containing prep wastes have exhibited reasonable chemical and physical properties and have the potential for use for general construction purposes.

The issue of high sulfur content in the prep waste has been addressed by making use of alkali-rich cement kiln dusts as an additive, whereby the alkali will react with sulfate in prep waste and “lock” them in the clinker, thereby precluding excessive potential sulfur dioxide stack emissions. The sulfates in clinker appear to exist as a calcium langbeinite compound that could contribute the same set regulating effect as gypsum in ordinary cement. It may be noted that calcium langbeinite contains three moles of sulfate for each mole of potassium. Because it can regulate set on its own, these clinkers would not require any gypsum addition.

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

Depending upon the substitution rate of the prep wastes, moderate amounts of residual carbon (about 25%) can be beneficial as fuel energy, but higher contents of coal may generate undesirable excessive heat in the early pyroprocessing stage. Similarly, the issue of combustible organics in the prep wastes also needs to be resolved at some point. One way of addressing the issue would be by reducing the addition rate of prep wastes so that the net amount of combustibles becomes too small to be regarded as a potential emission issue.

Overall, this concept of converting prep wastes into cement in conjunction with CKD, will positively address the issues of waste management and related environmental stresses faced by the coal mines and cement plants in Illinois. Both industries would benefit economically as well as environmentally in adopting this concept. A full-scale demonstration is recommended to assist in demonstrating these benefits.

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EQUIPMENT INVENTORY REPORT  
November 1, 2001 through October 31, 2000

Project Title: **CONVERTING ILLINOIS COAL PREP WASTES INTO  
SUPPLEMENTARY PORTLAND CEMENTS**

ICCI Project Number: 01-1/3.1D-2  
Principal Investigator: Javed I. Bhatti, CTL, Inc.  
Other Investigators: John Gajda, and F. M. Miller, CTL, Inc.  
ICCI Project Manager: Francois Botha

**List to of Equipment Purchased**

No equipment was purchased for this project.

PUBLICATIONS AND PRESENTATIONS REPORT  
November 1, 2001 through October 31, 2000

Project Title: **CONVERTING ILLINOIS COAL PREP WASTES INTO  
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ICCI Project Manager: Francois Botha

List of Publications and Presentations

No publications or presentations were made on this project.