

AMENDING COAL REFUSE WITH ALKALINE MATERIALS

By

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ABSTRACT: Initially started in 1987 on one refuse area, the use of alkaline amendments for preventing Acid Mine Drainage (AMD) in coal refuse was instituted in earnest by the West Virginia DEP Office of Mining and Reclamation, Oak Hill office, in 1993. An overview of the data required to assess the potential of the refuse to produce AMD, the types and application of different types of amendment used and the results to date on the water quality of the discharges are discussed. This method has, to date, allowed the recovery of coal resources that might otherwise be too toxic to mine and refuse in an environmentally acceptable manner.

DISCUSSION: The first objective of evaluating what amendment may be required in neutralizing coal refuse, is to quantify the acidic potential of the material in question. Several different techniques have been used to quantify the nature of the refuse and the amount of alkaline material that would be required to neutralize the AMD (Acid mine drainage). These techniques are (1) acid/base accounting (see Attachment 1) (2) column leaching (see Attachment 2a) (3) accelerated Soxhlet leachate testing (4) sulfur forms and quantifying the pyritic content of the refuse. All of these techniques attempt to predict the acidic production of the pyritic sulfur oxidation products, either empirically through leaching tests or, by predictive analysis of the theoretical total acid potential of the pyrite oxidation. In addition, other empirical historical and water data from adjacent correlatable geologic strata is used to predict the amount of AMD possible.

If the coal refuse facilities include an impoundment where the fine slurry refuse is segregated from the coarse refuse, then each component needs to be analyzed separately. This is because the size of the pyrite contained in the refuse could dictate significant differences in the pyrite content of the slurry and the coarse refuse (see Attachment 4). The amount of pyrite and its size is site specific to the coal seam and its depositional model. It has been observed that some coal seams contain more pyrite in the coarse size fraction, and some seams more pyrite content in the fine fraction.

The samples that are needed for the various tests can either be direct samples from an operating coal preparation plant or they can be constituted from exploration cores in the following manner (1) The company must provide a preparation plant flow sheet and the proposed specific gravity at which they intend to operate the coal preparation. It must also be determined whether or not a slurry impoundment will be used because it will require

sampling the coarse and fine refuse (2) At the proposed specific gravity, the entire mineable seam section should be float and sunk in the coal laboratory. The sink portion of this test represents the refuse portion of each coal seam. Each coal seam that is mined and prepared at the plant should be separated in this manner. It is important that the seam section analyzed be representative of the seam section to be mined, including all the coal partings, roof and floor that may be taken in the mining process and delivered to the preparation plant for washing (3) After the sink portion is separated in the analytical procedure, it should be tested for sulfur forms and acid/base accounting. From the sulfur form data we can determine the pyritic sulfur content which theoretically determines the total acid potential of a material and from the acid/base accounting we can evaluate the empirical data for the acidic/alkaline potential of the material.

The following criteria for evaluating the sample analyses (see Attachment 1), based on our experience and literature on the subject of AMD potential, suggests that:

1. -5 acidic (negative) CaCO₃ deficiency- amendment is definitely required.
2. -5 to +5 CaCO₃ equivalent-neutralization potential is borderline, further investigation of the area history, pyritic content of the refuse and other factors should be considered before a finding of no amendment required is reached.
3. +5 or greater CaCO₃ neutralization potential- no amendment is required unless there is compelling evidence to the contrary.

Initially we required the companies to do Soxhlet or longer term leachate testing at varying amendment percentages by weight, by seam and by type of amendment. After some trial and error it was decided that the Soxhlet leachate studies be conducted for at least 10 weekly cycles to stabilize the pH curve. Column leachate studies would probably be of even longer duration. In the interest of obtaining analogous results to the leachate studies in a more expeditious and cost effective manner, we compared the amount of amendment required for neutralization as indicated by the leachate studies, and the amount of amendment required by the formula $\%S(\text{pyritic}) \times 3.125 \times .75(\text{NP})/\%CaCO_3 \text{ equivalent} = \text{Amendment } \% \text{ by weight}$. This formula is a composite of previously proposed ways to calculate the amount of neutralization quantity needed based on stoichiometric equations for neutralization. The results of the calculation by formula and by leachate studies indicated a close correlation of the final amendment percentage estimated by both methods. The formula method was selected as the currently suggested method of calculating the amendment percentage required in the refuse. This method was not only cheaper and more expeditious than leachate studies, it was also selected for other important reasons (1) the laboratory test for sulfur forms is an ASTM Standard test that has been used for around a century while the Acid/Base analyses and the Soxhlet leachate tests are not performed to ASTM Standards and are not repeatable to the extent required (2) Because the amount of pyritic sulfur in a coal seam is a standard analysis for (a) preparation plant design (b) coal quality parameters for sales (c) used to evaluate prep plant efficiency in sulfur removal, the amount of data, even from older core holes, etc. is considerable and would be statistically much more significant than the leachate studies which use very small and spatially insignificant samples that are not indicative of the coal seam to be mined and refused (3) the amount of pyritic sulfur in the coal is a parameter that is, in most cases, an analysis that is already available from operations and can be used as a monitoring parameter to make sure the amendment percentage being used is commensurate with what percentage is required.

The final amendment evaluation should include the following:

1. All analyses and study results to include any leachate studies, sulfur form analyses, acid/base analyses, mineral analyses and any other historical water data, etc. on each coal seam that will be refused.
2. Amendment percentages that are proposed from the formula or the leachate studies. The amendment percentage approved in a multi-seam operation should be based on the seam with the highest pyrite content and the highest acid potential. Only if the applicant can categorically state that an everyday consistent blend of seams (on the raw coal side) is to be performed, or if the seams are always run individually for longer periods, should any deviation in using the worst seam for the amendment percentage be contemplated.
3. A specific mineral analysis and TCLP metals analysis should be included for any amendment type(s) that is proposed by the applicant (see Attachment 7c). These analyses will indicate if any of the amendment types contain any undesirable constituent that would be environmentally harmful if it leached from the amendment (we do not want to make the "cure" worse than the "disease"). The amendment types that have been used in our area include (1) limestone sand (2) calcium oxide (3) kiln dust (lime) (4) Magnalime (fluidized bed ash based on dolomitic limestone) (5) calcium hydroxide (6) hydrated lime (7) dolomitic steel mill slag (8) etc., etc. Each of these products have their own advantages/disadvantages in the speed of the neutralization reaction, the cost of the material, the handling characteristics and the availability of the material. Some of the products were waste materials with little or no value until they were used in the refuse amendment process. We have not confined an applicant to one amendment type. The only requirement is to change the percentage amendment rate according to the calcium carbonate equivalency of the material.
4. A schematic and plan view of how the amendment will be blended with refuse (see Attachment 8a). The blending is very important and should be on the plant refuse belt or slurried with the fines as they leave the plant. There should be some consideration given to picking the right amendment for the weather conditions (ie freezing, etc.).
5. A daily chart showing the amount of refuse processed (by weight), the amount of amendment added and a signoff block for plant management. This plan was formulated with the I & E inspectors who needed a method of checking to see that the proper amount of amendment is being used. This chart should be posted at the plant and available for DEP inspection.

OBSERVATIONS: Over sixteen (16) new and existing refuse areas now have a refuse amendment program in place. They are presently using an alkaline refuse amendment in combined refuse areas, impoundments where both the coarse and fine fractions are amended at different rates and with slurries that are injected underground. The alkaline products used for the amendment range from 78% CaCO₃ limestone sand to Calcium oxide with a CaCO₃ equivalency in excess of 110%. The main determination on selection has been made on price and availability. The companies have to balance the amount of CaCO₃ equivalency in the product with its price. A rule of thumb cost for the refuse amendment is approximately \$0.25/ % amendment/clean ton of coal produced (at approximately a 50% recovery rate). The sizing of the material and its surface area available for reaction is also a determining factor in

the selection of the amendment. Very fine material such as kiln dust and calcium oxide have high neutralization effects and are disseminated very quickly into the refuse environment, however they are much more difficult to handle in all weather conditions and the calcium oxide in particular presents some worker hazards in handling because of its caustic nature. The finer material would also be consumed much more rapidly in the neutralization process, while a material such as limestone sand would react slower but be more effective over a longer period. Some companies have used a combination of a stronger, finer neutralizer on the front end and then used limestone sand after the first few months of refuse placement. It is critical that the alkaline amendment in new refuse areas be started at the very beginning, because the lower parts of the refuse pile will be the areas that will be below the phreatic level once the water table regenerates in the pile. An additional benefit of an alkaline amendment is the better ground stabilization that occurs from the pozzolanic effect of the alkaline amendments, particularly in the combined refuse piles which contain a large moisture percentage from the fine coal fraction.

All of the refuse areas that have been treated with an alkaline amendment from initial refuse placement, have exhibited pH's in the +6 to 8 range without any additional treatment (see Attachments 10a and 10d). Four other refuse areas that started using refuse amendments late in their history have also seen water quality improvements. We have one mine complex in Nicholas County, WV that has two refuse areas that are adjacent to each other that have refused the same coal seams, with the older area only amended in its last year of life and the new area amended from the first refuse placement (see Attachment 11). Whereas the older refuse area needed heavy treatment with caustic soda and other neutralizers to meet the +6 pH limit, the new area exhibits +/- 7 pH with relatively low metals. The differences in the Iron and Manganese concentrations are dramatic between the two refuse areas and the pH is consistent in the new refuse pile. The consistency is important for the treatment of the older pile, because the company used so much caustic soda at times to neutralize the pH and get the metals (ie FE & MN) in compliance, that the pH upper limit of 9 was periodically exceeded and the amount of sludge became a significant problem in pond capacity and the sludge's disposal. The added benefit of metals reduction in the new pre-treated refuse area has replaced the costs from caustic soda or other treatment at the outlet that was performed on the old refuse area, and has produced a significant cost benefit for the pre-treatment method versus the post treatment traditionally used to increase pH and reduce metals. In addition to monitoring the water from the amended refuse areas, a number of samples per lift (ie. 2' compacted) were taken and run for NP and pH (see Attachment 12). Although the results over a large data set could be correlated to an average .75 NP, the individual analyses of the refuse with the amendment (as placed) was very inconsistent, which is attributable to the size distribution of the samples, and the virtual impossibility of the sampling technician to obtain consistent samples.

All of the refuse areas that have been pre-treated from their inception with an alkaline amendment have exhibited consistently acceptable water quality, some for several years. The older refuse areas, that have experienced alkaline pre-treatment in their later years, have have seen improving discharge water quality from these piles.

CONCLUSIONS: The following conclusions and implications can be drawn from the observations made on alkaline pre-treated refuse:

1. The pre-treatment of moderately acidic refuse with alkaline amendments has been

successful in the short term (i.e. +-5 years) and would appear to be a medium term (i.e. +- 10 years) solution to treat refuse with the potential to create AMD. The long term (i.e. + 20 years) solution is still a moot question. With good placement techniques (compaction) and the pozzolanic effect of the alkaline amendment solidifying the refuse to decrease water infiltration, it is likely that the pre-treatment of acidic refuse offers a good possibility of a permanent solution to AMD from refuse areas.

2. The use of the formula $[\%S \text{ (pyritic)} \times 3.125 \times .75(\text{NP}) / \% \text{ CaCO}_3 \text{ content of the alkaline amendment} = \text{the weight percent of amendment required}]$ has been effective in determining the amount of alkaline material required to neutralize the acid potential of the refuse. The analytical data required, (1) the pyritic sulfur content of the refuse and (2) the Calcium carbonate content of the amendment, is obtained by ASTM standard tests and the pyrite data represents a more statistically, spatially and scientifically acceptable method of determining the acidic potential of the refuse. The pyritic content of the coal seam can be gathered from a number of sources and is available in a number of historical data sheets.
3. Proper blending of the amendment material with the refuse should be on the refuse belt at the preparation plant to insure adequate distribution of the amendment and provide alkaline neutralization before the refuse has a longer period of time to oxidize. Layering the refuse by bulldozer on the refuse pile itself should be discouraged as a long term solution to amendment addition. In amending slurry the process is similar except the amendment would be added to a stream containing approximately 30% solids and 70% moisture.
4. An added benefit of the alkaline amendment is the pozzolanic effect, which significantly enhances the handling characteristics of the moisture laden combined refuse.
5. Any alkaline material with neutralization capabilities can be used in this process of amending the refuse. The amount of amendment required is based on the calcium carbonate equivalent of the amendment. The sizing is an important factor in which amendment is chosen and should be fine grained (i.e. sand size or less) to realize the benefits of the neutralization capabilities of the material.
6. Capping off refuse areas with water problems seems to help increase the pH and improve the water quality. No matter how late in the life of a refuse area, alkaline amending the refuse provides some water quality benefits.

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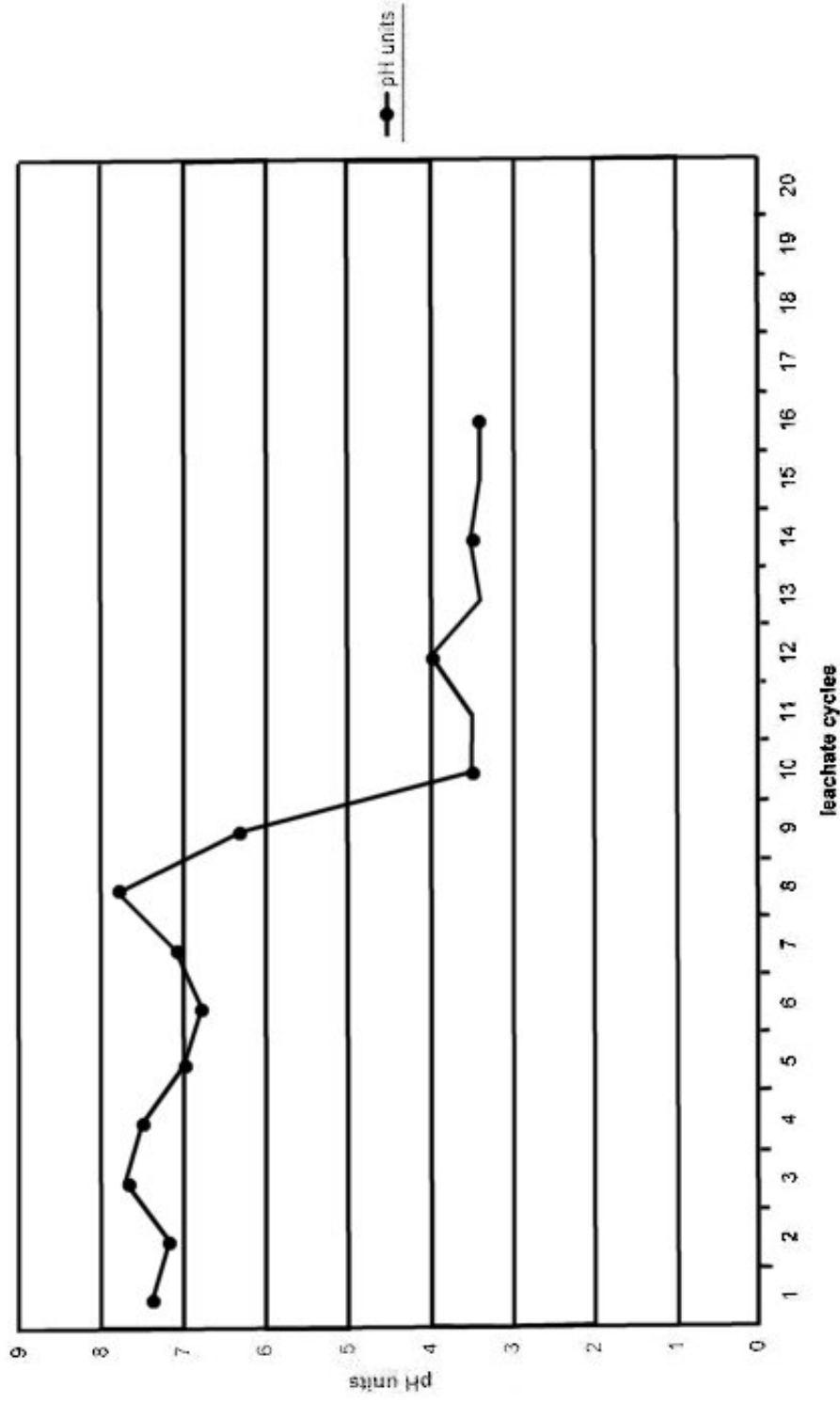
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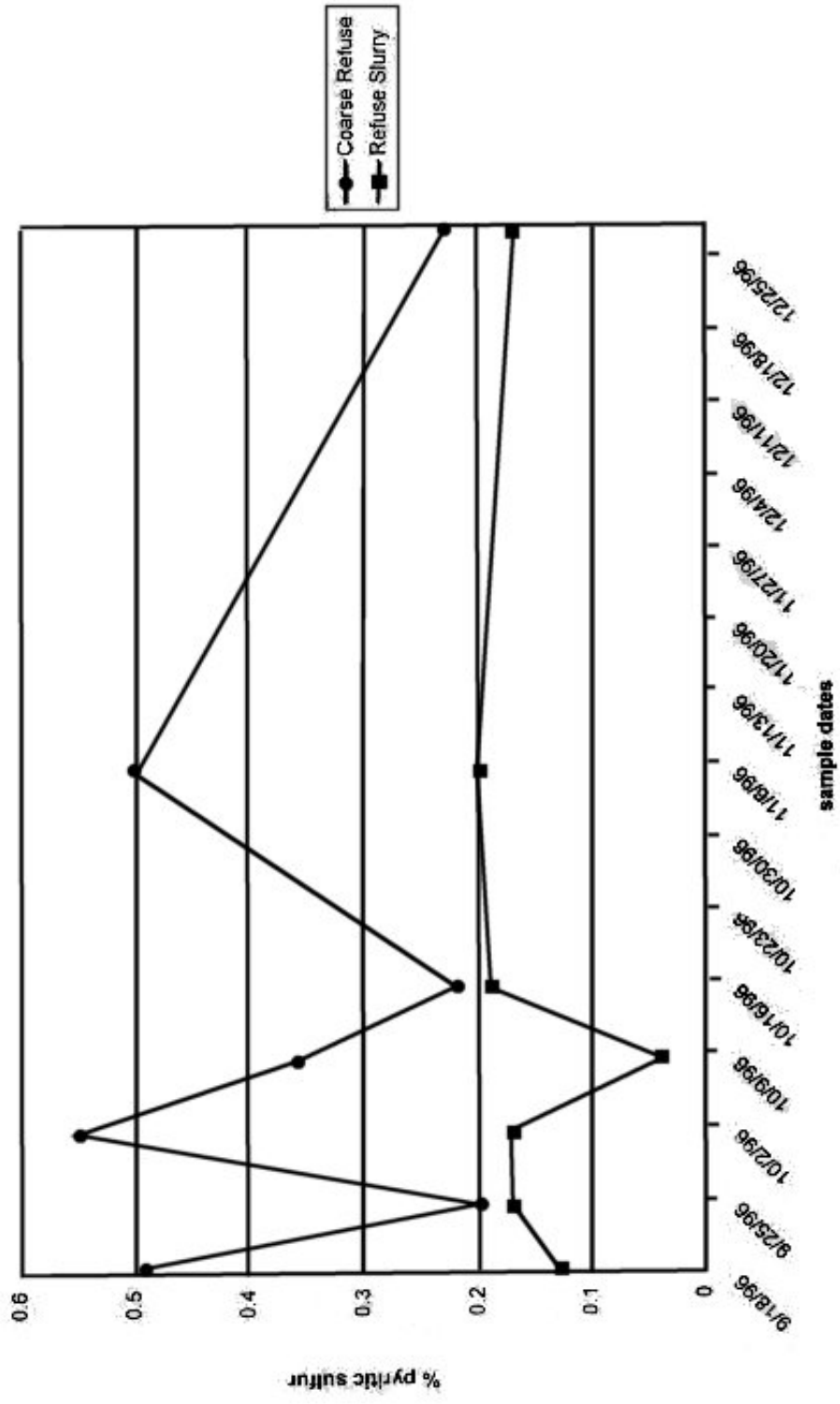
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Eagle Refuse



ATTACHMENT 2A

Eagle Seam- Coarse vs Fine Refuse pyrritic sulfur





Laboratory Analysis Report

Pete Gove
MOUNTAIN STATE COMPANY

Laboratory Number 298-07-0494-001 Respectfully
Submitted:

STEEL SLAG
BRADFORD

Date Sampled 07/16/98 12:42
Date Received 07/16/98

Sampled by CLIENT

073098 1655

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE:METALS

ANALYZED PARAMETER	CAS NO.	RESULT	LOG (MG/L)	METHOD	REGULATORY LEVEL	DATE/TIME/ANALYST
Metals - TCLP Basis						
Arsenic (As)	7440-38-2	ND	0.10	SM6010	5.0	07/24/98 10:29 JJ
Barium (Ba)	7440-39-3	ND	2.0	SM6010	100	07/24/98 10:29 JJ
Cadmium (Cd)	7440-43-9	ND	0.020	SM6010	1.0	07/24/98 10:29 JJ
Chromium (Cr)	7440-47-3	ND	0.050	SM6010	5.0	07/24/98 10:29 JJ
Lead (Pb)	7439-92-1	ND	0.10	SM6010	5.0	07/24/98 10:29 JJ
Selenium (Se)	7782-49-2	ND	0.20	SM6010	1.0	07/24/98 10:29 JJ
Silver (Ag)	7440-22-4	ND	0.020	SM6010	5.0	07/24/98 10:29 JJ

ND: Not detected at a concentration greater than the LOQ - Limit of Quantitation.

Method Reference: USEPA: Test Methods For Evaluating Solid Waste; SW-846, 3rd Edition; Nov 1986.

TCLP Extraction Procedure and Regulatory Levels: 40 CFR Part 261.24 and Appendix II.

ATTACHMENT 7C

4665 Paris Street, Suite 200-B, Denver, CO 80239 - Tel: (303) 373-4847 Fax: (303) 373-4884
1258 Greenbrier Street, Charleston, WV 25311-1002 - (304) 346-0725 Fax: (304) 346-0761
5712 Erdman Ave., Baltimore, MD 21205-3599 - Tel: (410) 483-2200 Fax: (410) 483-2206
4440 Glen Este-Wilhamsville Road, Suite 900, Cincinnati, OH 45245-1331 - Tel: (513) 752-9696 Fax: (513) 752-2014

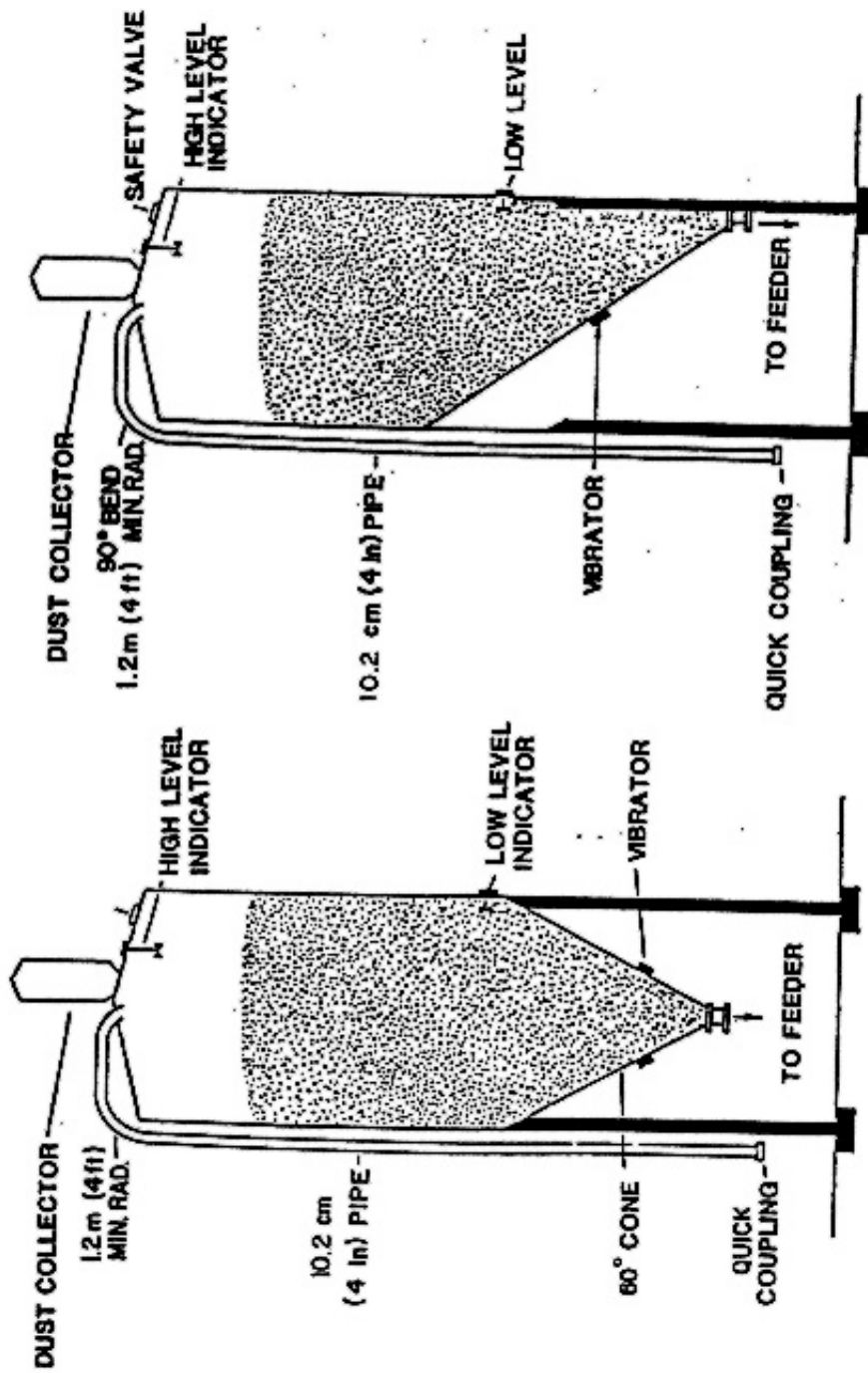
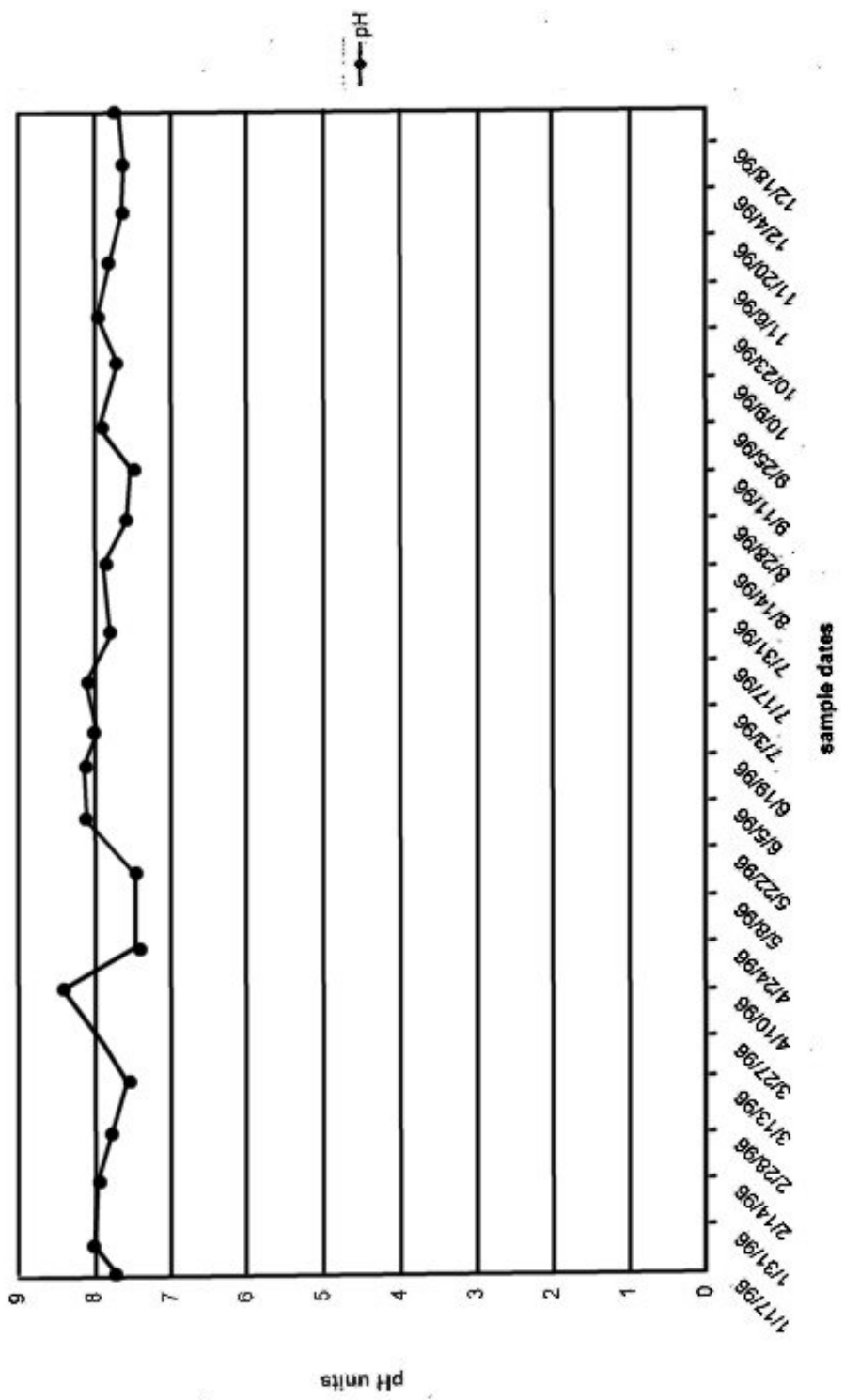


Figure 3-3. Standard and offset hopper bottoms.

ATTACHMENT 8A

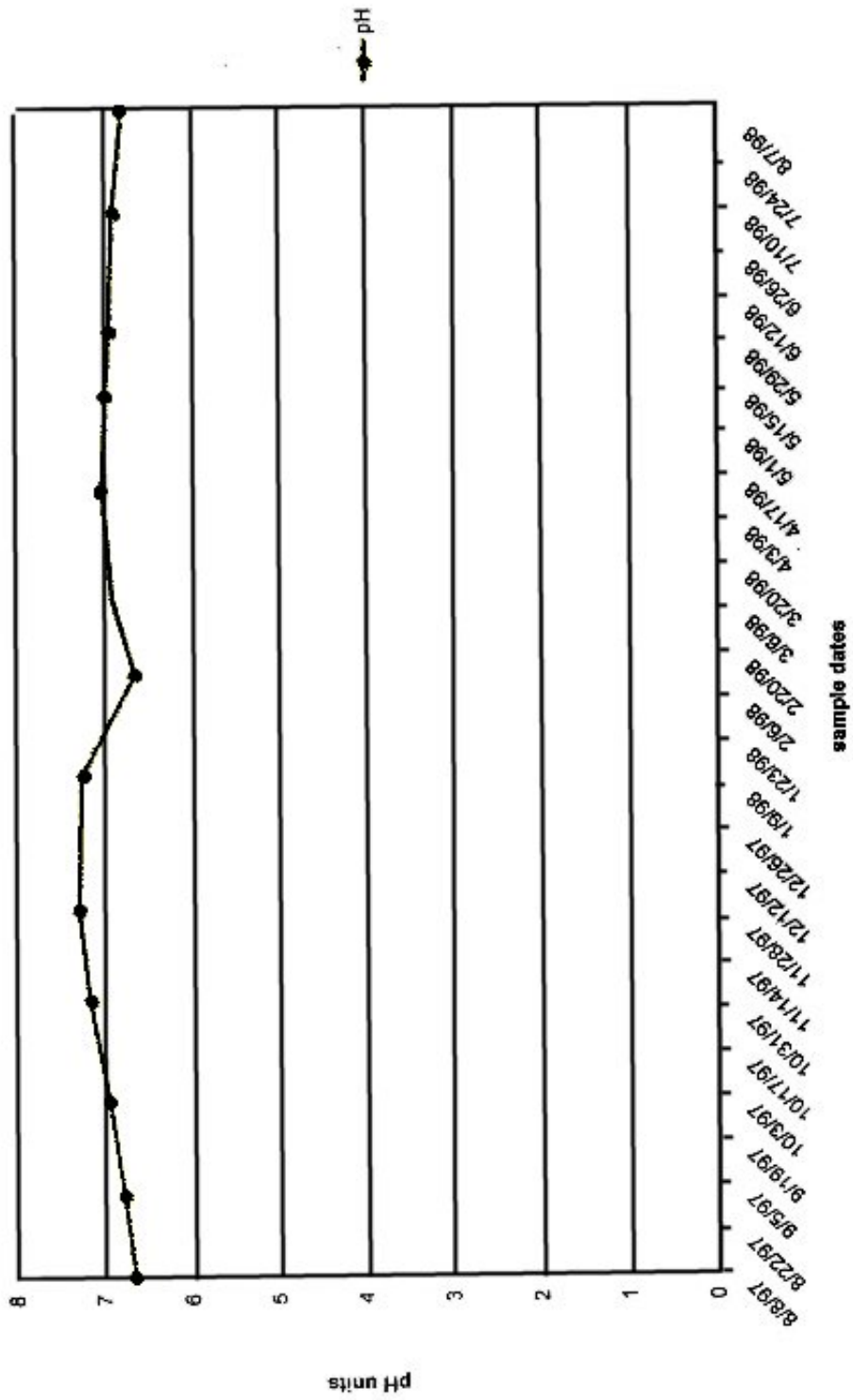
A-8a

Raleigh Co. Combined refuse Amended

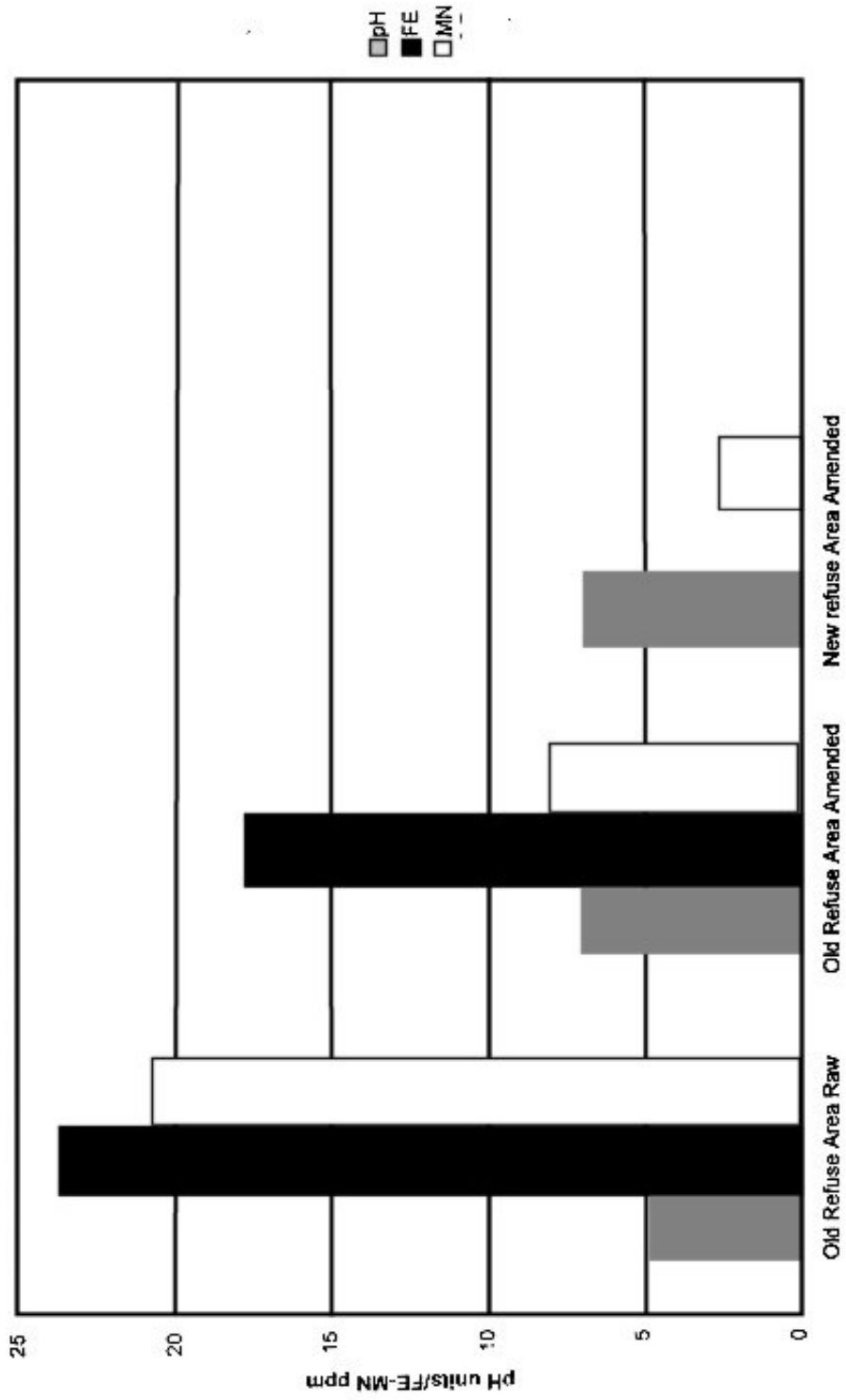


ATTACHMENT 10A

Nicholas Co. Refuse Permit Amended



Nicholas County Refuse Area Comparison



NPMPACH.XLC

NP/MPA RATIO TRACKING CHART

AN NP/MPA RATIO OF .75
IS DESIRED.

NOTE: SAMPLE 18 (SAMPLE 8 ON MAY 18)
WAS DELETED DUE TO AN INCORRECTLY MARKED REGION OF 18.9

