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An Assessment of Alkaline Addition on Reclaimed Surface Mines in Pennsylvania – 2019

PA Dept. of Environmental Protection

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Purpose and scope of study

The importation of alkaline material, chiefly waste lime, in surface mine backfills to compensate for alkaline-deficient overburden has become an increasingly common practice, particularly as coal reserves with alkaline overburden have been mostly exhausted. As highly alkaline-deficient sites are increasingly proposed for mining, higher alkaline addition rates on the order of 1,000 to 3,000 tons per acre, once very rare, are becoming commonplace. This has led to concerns that very high alkaline addition rates may result in excessive levels of total dissolved solids (TDS) in postmining drainage and receiving streams. In Pennsylvania, NPDES limits are based on osmotic pressure (OP) rather than TDS. The Chapter 93 osmotic pressure in-stream criterion is 50 milliosmoles per kilogram (mOsm/kg). Predicting postmining OP is an important factor in the review of probable hydrologic consequences of mining, and the setting of appropriate NPDES effluent limits. However, it was recognized that OP was never adequately studied in relation to alkaline addition. Accordingly, the principal purpose of this study was to examine a large number of issued surface mining permits which employed alkaline addition in order to assess its relationship to OP.

A secondary, albeit just as important, reason for this study was to reexamine the effectiveness of alkaline addition in preventing acidic drainage and in its impact on postmining water quality. It has been more than 20 years since the issuance of technical guidance for alkaline addition and the discussion of it in Pennsylvania's Coal Mine Drainage Prediction and Pollution Prevention manual (CMDPP). No systematic review of alkaline addition sites has been performed since. How well has alkaline addition worked? Are there any observations that can be made or conclusions that can be reached concerning the appropriate application rates? Although this study was chiefly designed to examine the link between alkaline addition and OP, additional observations may be useful.

Background

The use of alkaline addition to prevent or remediate acidic drainage was first reported in 1980 at a fill along Interstate 80 (Waddell, et.al.). It was largely ineffective due to the low surficial application rate. Similar results were obtained by Lusardi and Erickson in 1985 at a site in Clarion County. By the late 1980's it was being tried as an experimental practice on several surface mining sites by applications both to the pit floor and within the spoil. Brady and others (1990) found that only higher rate (+500 tons/acre) applications had been successful and that applications solely to the pit floor or spoil surface mostly failed. In 1995, Rose et.al. studied a Clearfield County site in great detail. Early success looked encouraging, but the site ultimately failed due to the application rate being too low.

Although not specifically related to alkaline addition, Brady and others (1994) examined the relationship between sulfur content, neutralization potential, and postmining water quality. This became the seminal study on how to interpret acid-base accounting. They concluded that the chief factor in determining whether or not postmining drainage would be alkaline or acidic was net neutralization potential (NNP), not sulfur content, and that excess NNP was needed in order to assure alkaline drainage. A NNP of 6 tons per thousand tons calcium carbonate equivalent or greater was considered as an assurance of alkaline drainage, if one applied threshold values of 30 for NP (with a fizz) and 0.5% for sulfur content, such that strata having values less than this would not be calculated in the NNP summation. If threshold values were not applied, a NNP of 12 (or 1.2% $CaCO_3$) was considered to be the safe level. Lower NNP values may or may not result in alkaline drainage. NNP values less than zero were almost certain to produce acidic drainage. Figure 1 shows graphically the results of the Brady study. Each mine site is represented by a single point which integrates the site-wide NNP and resulting postmining alkalinity.

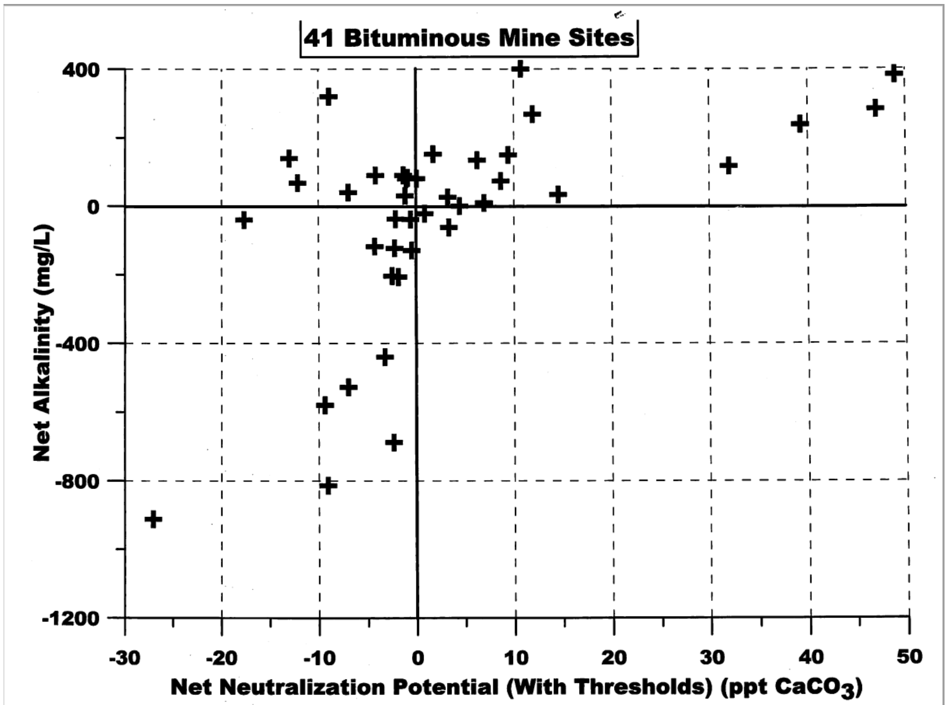

Figure 1. Net alkalinity of postmining water quality as a function of premining NNP, from Brady, et.al. 1994.

In 1998, Smith and Brady, applied the acid-base accounting study to alkaline addition rates, suggesting that calcium-carbonate based imported alkaline material acted in the same manner as naturally alkaline overburden. Therefore, if alkaline material was imported at the rate necessary to achieve the NNP indicated by Figure 1; and provided that the alkaline material was thoroughly incorporated into the backfill like naturally alkaline overburden, then the same postmining water quality would result. This became the basis for the Department's recommendations for alkaline addition and is manifest in the 1997 technical guidance for alkaline addition at surface coal mines. The technical guidance recognized that this was still an emerging practice with more needed to be learned and that application rates that achieved a NNP in the range of 0 to 6 (with thresholds applied) are not assured to produce alkaline drainage. Further, it was not known how the production of metals would respond to alkaline addition. Because of this uncertainty, alkaline addition was not allowed as a practice in special protection watersheds or wild trout streams if the permit was not otherwise issuable. Additional monitoring was also called for on these sites, in the form of backfill monitoring wells or specific monitoring points that would directly encounter water from the backfill, to provide a better understanding of the efficacy of alkaline addition in preventing acid mine drainage.

Following the initial technical guidance on alkaline addition, several failures of alkaline addition at rates less than those needed to achieve NNP = 6 were noted. This led the DEP to propose changes to the guidance, which further limited the conditions where a NNP<6 alkaline addition rate would be considered. That revised technical guidance document was published as final in August 2020.

Procedure

Bituminous District Mining Offices (Cambria, Knox, Moshannon, and New Stanton) were asked to submit candidate sites from permits issued during the last 20 years, that is, post-issuance of the original alkaline addition TGD and the publication of the CMDPP manual. Candidates were requested that had significant alkaline addition rates (greater than the BMP rate of 200 tons per acre), and good monitoring data with monitoring points that received all or most of their water from the alkaline addition area which would effectively show its impact. Each of the proposed sites was reviewed in detail; however roughly half of the sites were rejected for several reasons: some were alkaline redistribution sites which was beyond the scope of this study; some had alkaline addition at rates less than or equal to 200 tons per acre; some were Subchapter F (remining) sites where the preexisting discharge included mine drainage from a larger area – making it difficult to discern the impacts from the alkaline addition area. Many of the proposed study sites were rejected because the principal monitoring point either did not show any indicators of recent surface mining (chiefly increased sulfates and/or alkalinity) or the impact of the alkaline addition area was too dilute to be effective. Finally, some of the sites were rejected due to problems identified by district office staff, such as uncertainty as to whether the required alkaline addition rate was actually applied.

Alkaline addition rates are commonly not uniform throughout a surface mining permit area, with some coal seams or areas needing alkaline addition and others not requiring or needing alkaline addition at differing rates. This study looked at only those parts of the permit that required alkaline addition and had adequate water quality monitoring of the alkaline addition area. In many cases, more than one alkaline addition rate was used but the entire area reported to the assigned monitoring point. In these cases, a volume- or acreage-weighted alkaline addition rate representing the overall alkaline addition rate was used for analysis. Also, alkaline addition rates in tons per acre, the typical permit requirement, were converted to and expressed in pounds per cubic yard (lbs/yd). Expressing alkaline addition rates in lbs/yd corrects for differences due to backfill thickness. For example, 1000 tons per acre in a 100-foot thick backfill is effectively half of the rate compared to if the backfill was only 50-feet thick. Where possible, this conversion was made using the overburden tonnage data contained in the Module 7.4 overburden spreadsheets. Yardage was calculated as tonnage/1.75. However, in some cases the overburden tonnage was expressed on the overburden spreadsheet for simple columns or the permitted mining area did not correspond to the area shown in the spreadsheet. In those cases, the approximate average overburden thickness multiplied by the alkaline addition mining acreage was used to determine overburden volume and alkaline addition application rate in lbs/yd.

Each alkaline addition area was also characterized by its target NNP, i.e. the expected net neutralization potential to be achieved after the alkaline addition is included. Usually, but not always, the target NNP is identified in the permit documents. Aggregate target NNP was based on a volumetrically weighted average. Where NNP was calculated without using thresholds, NNP was divided by two to approximate the NNP with thresholds, which is roughly analogous to the Brady et.al. (1994) alkaline addition study that indicated alkaline drainage when NNP is 6 or greater with thresholds or NNP is 12 or greater without. Target NNP values ranged from 0 to 11.4 but were most commonly 6. NNP was divided into three classes: NNP in the 0 to 2 range; NNP greater than 2 but less than 6; and NNP greater than or equal to 6.

Ultimately, 44 sites were selected for the study. Forty-one of the study sites are distributed across the bituminous mining area, with a fairly even distribution by district: Cambria = 9, Knox = 13; Moshannon = 11; and New Stanton = 8. Summary data from the study sites are included in Appendix 1. Alkaline addition rates for the 41 mining study sites ranged from 205 to 3,000 tons per acre or 4.2 to 96.8 lbs/yard^3. Three additional unconventional alkaline addition sites were added that represented the highest known rates of alkaline addition: The Fran Contracting reclamation project, in Clinton County, is an abandoned mine site that was producing severe acid mine drainage and previous attempts at remediation were unsuccessful. Through a reclamation contract, BAMR completely re-excavated the entire 42 acres of backfill and mixed it with enough lime to achieve a NNP=12 without thresholds, or 4000 tons per acre.

The other two sites are part of the same project consisting of two separate landfill cells along I-99 in Centre County. At this project, known as the ERPA (Engineered Rock Placement Area), PennDOT re-excavated approximately 1 million yards of acid rock containing hydrothermally emplaced pyrite (and other sulfides) encountered at a large excavation mostly of the Bald Eagle Sandstone

Formation in Bald Eagle Mountain. The original fills produced severe acid rock drainage. As with the Fran Site, the acid-forming rock was re-excavated and mixed with waste lime and emplaced into two separate cells, complete with liners and leachate detection zones. Again, in the amount needed to achieve NNP=12 without thresholds, the alkaline addition rates for both cells was 400 $lbs/yard^3$ of rock, which equated to 9400 tons per acre. Because the ERPA site was composed of two separate individual cells with separate leachate collection and monitoring, they were treated as two separate alkaline addition sites.

At each site, a principal water quality monitoring point or points for the alkaline addition area was determined. They were usually identified by district office staff or in the permit document. The alkaline addition technical guidance calls for backfill monitoring wells unless other suitable groundwater monitoring points exist; however relatively few sites had backfill wells. Most relied on springs and seeps. Sites with monitoring points that exhibited no discernable “bump” in sulfate or alkalinity levels were excluded from the study for reasons explained below. The Fran and ERPA sites had constructed underdrains, an effective and direct method for monitoring water from the backfill. Median values for specific conductance (SC), total dissolved solids (TDS) when available, alkalinity, sulfate, iron, and manganese were obtained from company monitoring data and DEP samples for the most recent available year. Most sites had post-revegetation monitoring data. For very recently mined sites, data represent water quality shortly after backfilling. The median was used because it is a better measure of central tendency rather than the mean, which may be skewed by extreme high or low values (which is common in mine drainage). Median values for baseline (premining) data were also determined for comparison. For sites with multiple monitoring points, the median values were averaged.

Even with alkaline addition, a rather dramatic increase in sulfates can be expected following mining when sulfur-bearing rocks are disturbed. As with all surface coal mining, sulfate can be used as a good indicator of whether there is a robust hydrologic connection between the monitoring point and the backfill. Using median sulfate concentration as an indicator of hydrologic connection, seven monitoring points with less than 100 mg/L sulfates were considered to have too weak of a hydrologic connection to the mined area to be useful to assess effects on osmotic pressure, although they were still included in the list of sites studied. Data for each site are summarized in Appendix 1.

Osmotic Pressure

Osmotic pressure (OP) is the pressure which must be applied to a solution to prevent the flow of pure water across a semipermeable membrane. In practical terms, it is the pressure exerted by a solution of salts on cell membranes. It is measured in milliosmoles per kilogram (mOsm/kg). Water with too high a concentration of dissolved salts will cause water from cells to diffuse across the cell membrane, causing the cell to lose water and turgidity. Consequently, water with too high OP is harmful to aquatic organisms by causing them to dehydrate through osmosis. In lieu of a total dissolved solids (TDS) standard, Chapter 93 specifies an OP standard of 50 mOsm/kg., which is a more direct measure of the impact of dissolved salts on aquatic life.

Because OP is directly related to dissolved salts, it has a close correlation with SC and TDS. Cravotta and Brady (2015) compared OP with TDS and SC in 46 mine drainage discharges, both raw and treated, throughout Pennsylvania. In their study, they found a much better correlation, r-squared = 0.958, with SC than with TDS (r-squared = 0.778). They postulated that the better correlation between OP and SC was because both parameters are similarly influenced by ionic species with lower atomic weights that tend to be dissociated while TDS is more heavily affected by ions with greater molecular weights and that form ion pairs with major cations. Thus, OP tends to track SC more strongly than TDS. While SC is easily measured and routinely included with mine drainage chemical analysis, OP is not.

OP monitoring data were generally unavailable in permit files, but SC was routinely collected and reported. Given the unavailability of OP data and the good correlation between OP and SC, this study estimated OP values from SC. However, to verify and better define the relationship between OP and SC for untreated alkaline-addition discharges, the monitoring points for each of the study sites were resampled for OP, TDS, and SC. The regression equation for these data, with origin at 0, is OP = SC x 0.0105 (r-squared = 0.958). The regression line is very close to that obtained by Cravotta and Brady. This equation (Figure 2) was used to estimate OP for each site, except for the Fran site where post-alkaline addition SC data varied greatly. In that case, the single OP measurement taken as part of this study was used to characterize post-alkaline addition OP. Data from the OP/SC/TDS sampling are included in Appendix 2.

Effectiveness of Alkaline Addition

Although the principal purpose of this study was to examine the relationship between alkaline addition and OP, the large number of sites reviewed and the comprehensiveness of the data allows for several observations about alkaline addition. DEP mining permit files contain an abundance of empirical data that collectively present a powerful tool for studying water quality impacts of mining. Similar empirical studies became the basis for determining how to properly interpret acid-base accounting and to assess the success of Subchapter F in addressing preexisting pollutional discharges. Alkaline addition was very successful in assuring alkaline drainage, especially when sufficient alkaline material was applied to attain a NNP of 6 or greater. Conversely, of the 44 sites studied, only 5 produced net acidic drainage or failed to meet a Subchapter F pollution load standard (i.e., increased loadings of one or more pollutants). Of those 5 sites, 4 had a target NNP less than 6 (0 to 4) so it is likely that they just had insufficient alkaline addition. Only one acidic site applied enough material to achieve a NNP of 6. It was on the Lower Kittanning coal with a required alkaline addition rate of 1600 tons per acre. It is unclear as to why that site failed to produce alkaline drainage.

The alkaline addition sites in this study were mostly successful in assuring alkaline drainage, but they had much lower success in avoiding iron or manganese problems. Each of the study sites was assessed as to whether the principal monitoring point (or average monitoring point if there were multiple points) exceeded the §87.102 instantaneous maximum iron and manganese standards of 7.0 mg/L and 5.0 mg/L, respectively. An exceedance does not necessarily mean that an effluent violation occurred. For example, some of the monitoring points may be backfill wells or discharges that do not leave the permit area. Nonetheless, they provide a good indicator of the post-alkaline addition water quality from the backfill and whether it could potentially lead to an effluent violation or prevent bond release. Of the entire population of 44 sites, 19 had indications of potential metals exceedances (13 for Mn, 3 for Fe, 3 for both Mn and Fe). Manganese was the most prevalent indicator of metals problems, suggesting that while alkaline addition can usually assure alkaline drainage, it does not prevent manganese production in overburden that is otherwise prone to manganese problems. Iron appears to be a much less common problem, presumably because the pH that can be achieved in alkaline addition-treated backfills is within the range that can cause iron to precipitate within the backfill or underlying strata. It is further noted that some monitoring points, such as backfill wells or underdrains, receive water directly from the mine spoil with little or no opportunity for contact with oxygen, degassing of CO_2, or precipitation of metals.

Alkaline Addition and Osmotic Pressure

One of the principal objectives of this study was to determine the level of alkaline addition at which there may be a significant risk that the postmining OP standard of 50 mOsm/kg may be exceeded. To do this, postmining OP was plotted against the alkaline addition rate. Alkaline addition rates were expressed both in tons per acre of mining area and in pounds per yard of overburden. As with the Brady et.al. (1994) study, considerable data scatter was observed, which is to be expected given the problems inherent in summarizing large mining areas having variable overburden characteristics with a single number, and with using water quality monitoring points that may reflect groundwater from areas other than just the alkaline addition area. Further, since the main premise behind alkaline addition is to replicate naturally alkaline rock, the water quality data are also affected by naturally occurring carbonates in the overburden. Nonetheless, some trends could be noted.

For this analysis, relatively minor alkaline addition rates less than 500 tons/acre or 10 lbs/yard³ were excluded. Also, monitoring points that did not show a median sulfate concentration of at least 100 mg/l were considered to be too dilute or weakly connected to the mining area to be effective indicators of post-alkaline addition water quality. This left 30 mine sites for analysis.

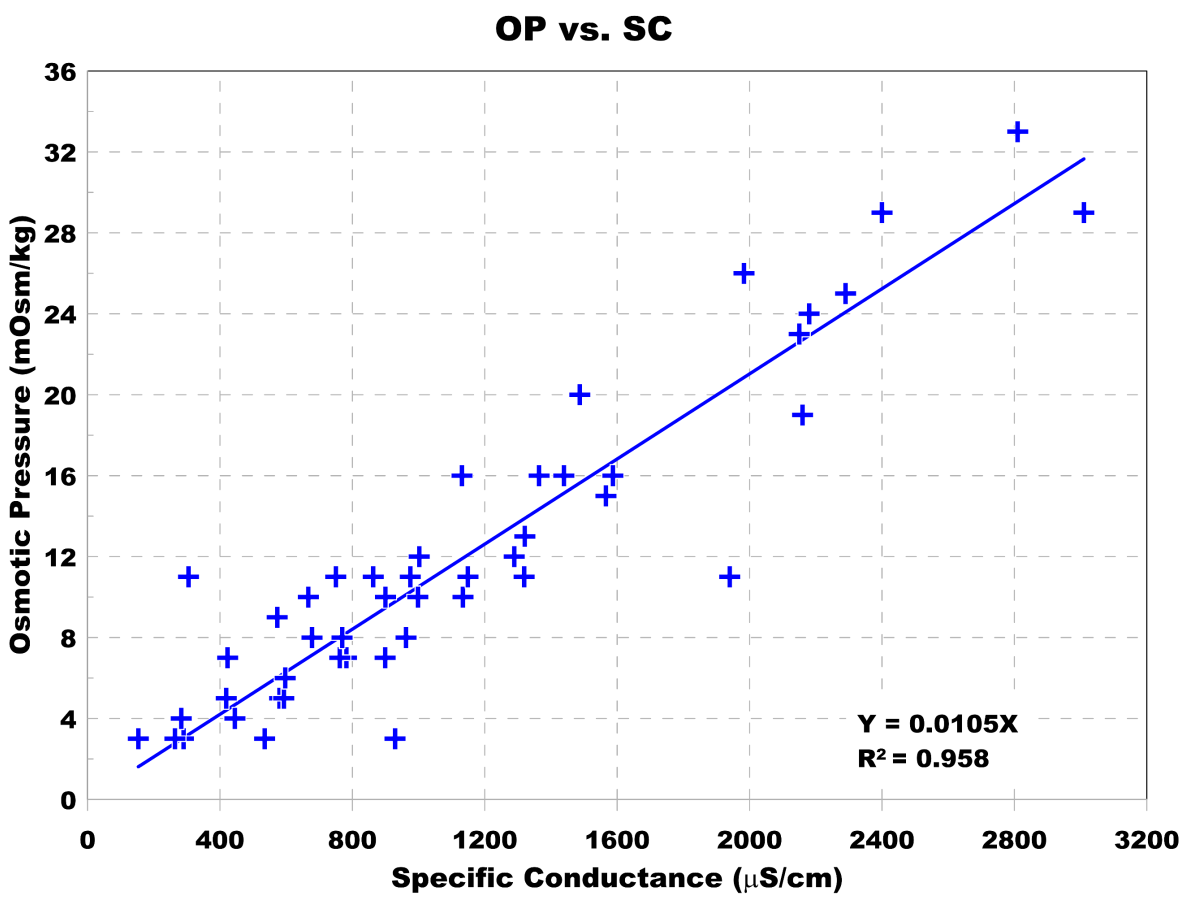

Figure 2. OP versus specific conductance for alkaline addition study sites.

As expected, OP was found to increase with increasing alkaline addition rates. Although there is considerable scatter, the best correlation (r-square = 0.486) was found when the alkaline addition rate in tons per acre was plotted with alkaline addition rate on a log scale. This suggests that higher alkaline addition rates may be subject to solubility constraints or geochemical processes that create a diminishing impact on OP. Surprisingly, plotting alkaline addition rates in lbs/yard³ rather than tons per acre made little difference in the strength of the correlation. Figures 3 through 6 show OP plotted against the alkaline addition rate in tons/acre and lbs/yard³. Significantly, no exceedances of the 50 mOsm/kg OP criterion were noted, even at the very high alkaline addition rates of 4,000 and 9,400 tons per acre or 310 - 400 lbs/yard³ with the monitoring point directly at an underdrain from the backfill area. So most alkaline addition areas are very unlikely to trip the OP limit of 50 mOsm/kg. Figure 7 shows the distribution of OP for sites with relatively modest (500-1,000 tons/acre) versus higher alkaline addition rates of 1,001-2,000 tons/acre and over 2,000 tons per acre. The median OP for the low application rate mines is 10.75 mOsm/kg compared to 14 mOsm/kg for medium application rates and 20.5 mOsm/kg for the highest application rate sites.

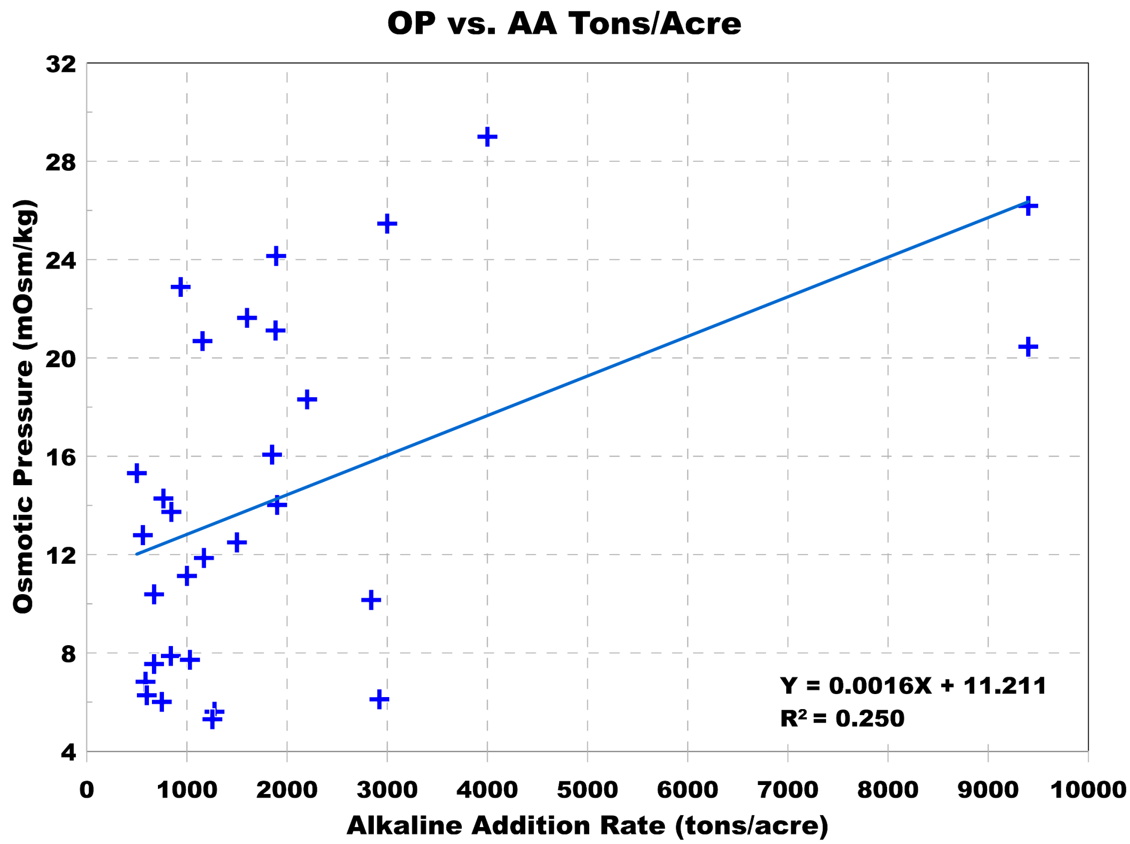

Figure 3. OP as a function of alkaline addition rate in tons per acre.

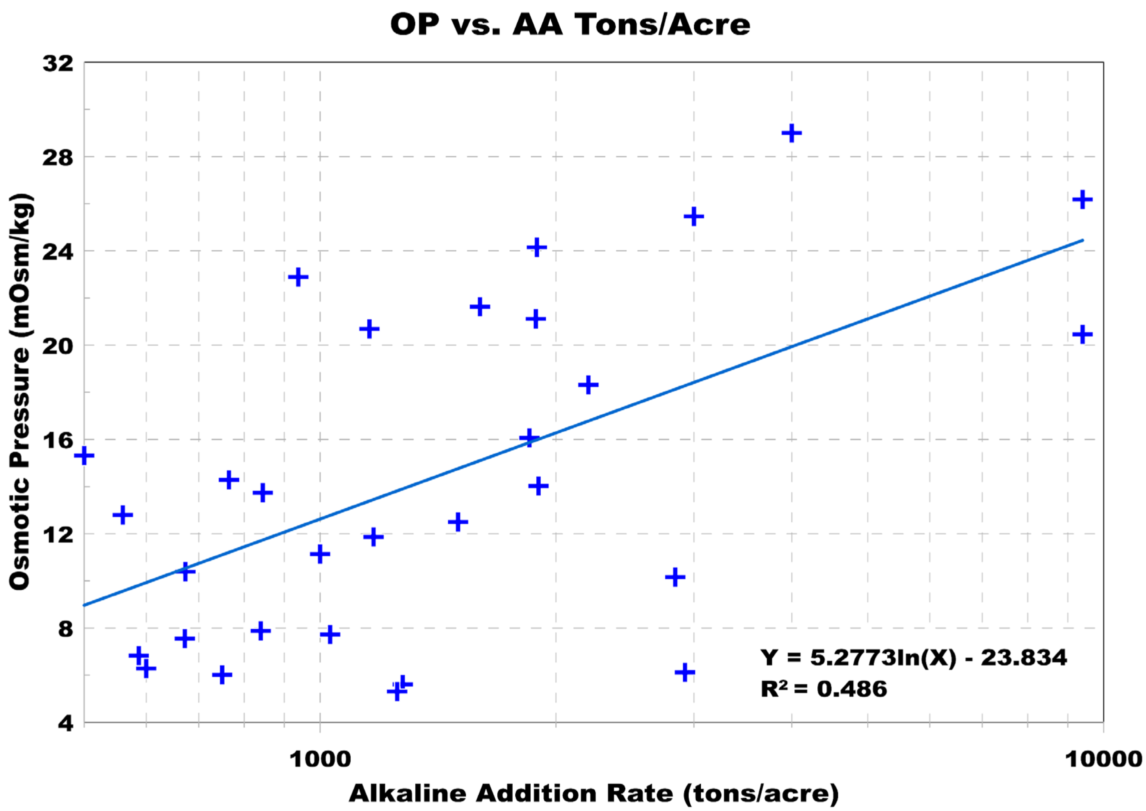

Figure 4. OP as a function of log alkaline addition rate in tons per acre.

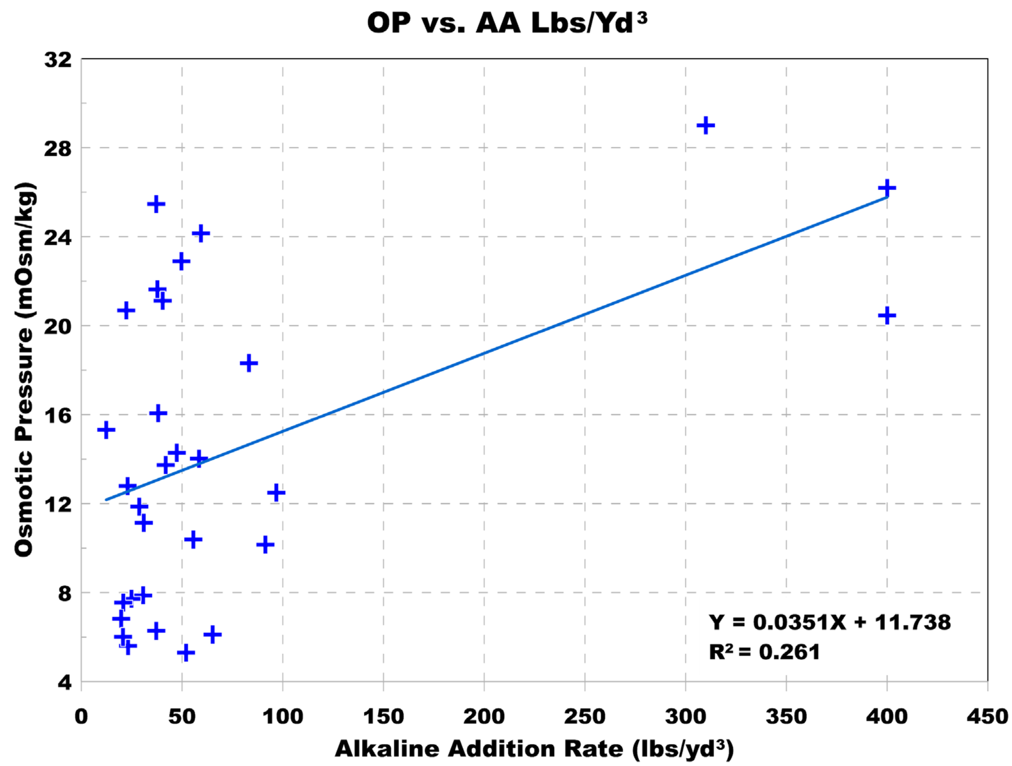

Figure 5. OP as a function of alkaline addition rate in pounds per yard.

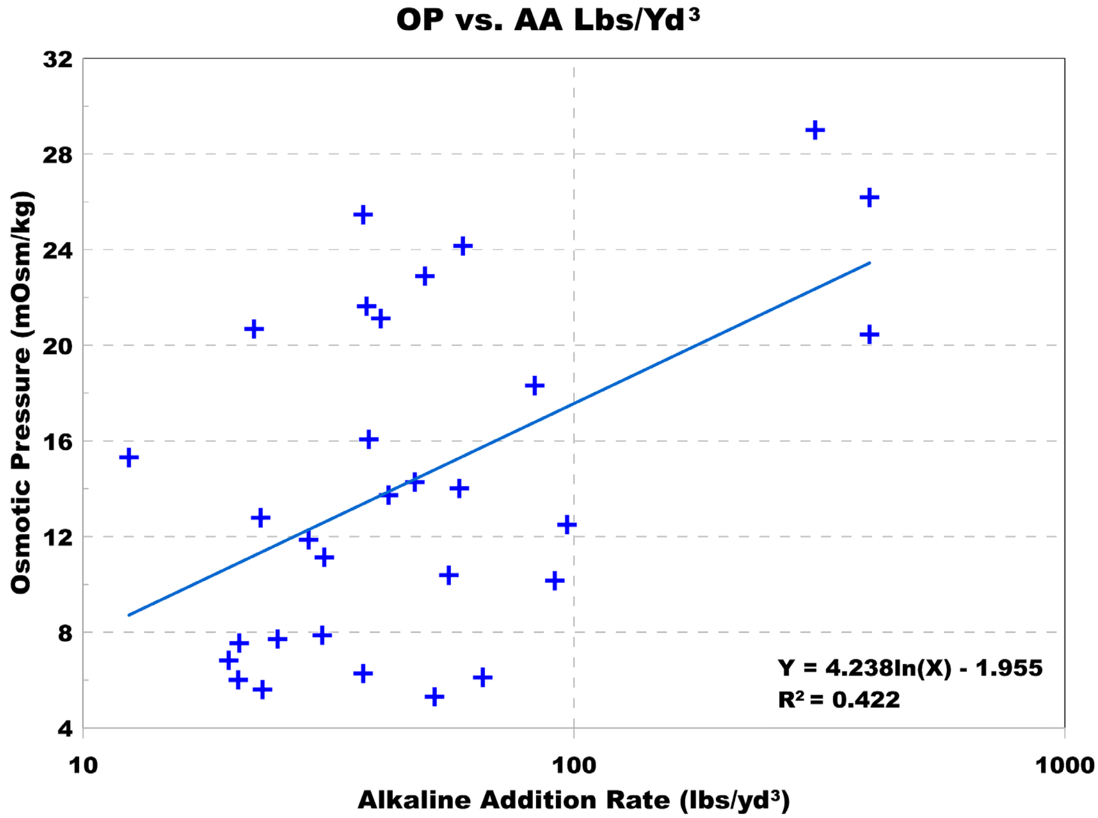

Figure 6. OP as a function of log alkaline addition rate in pounds per yard.

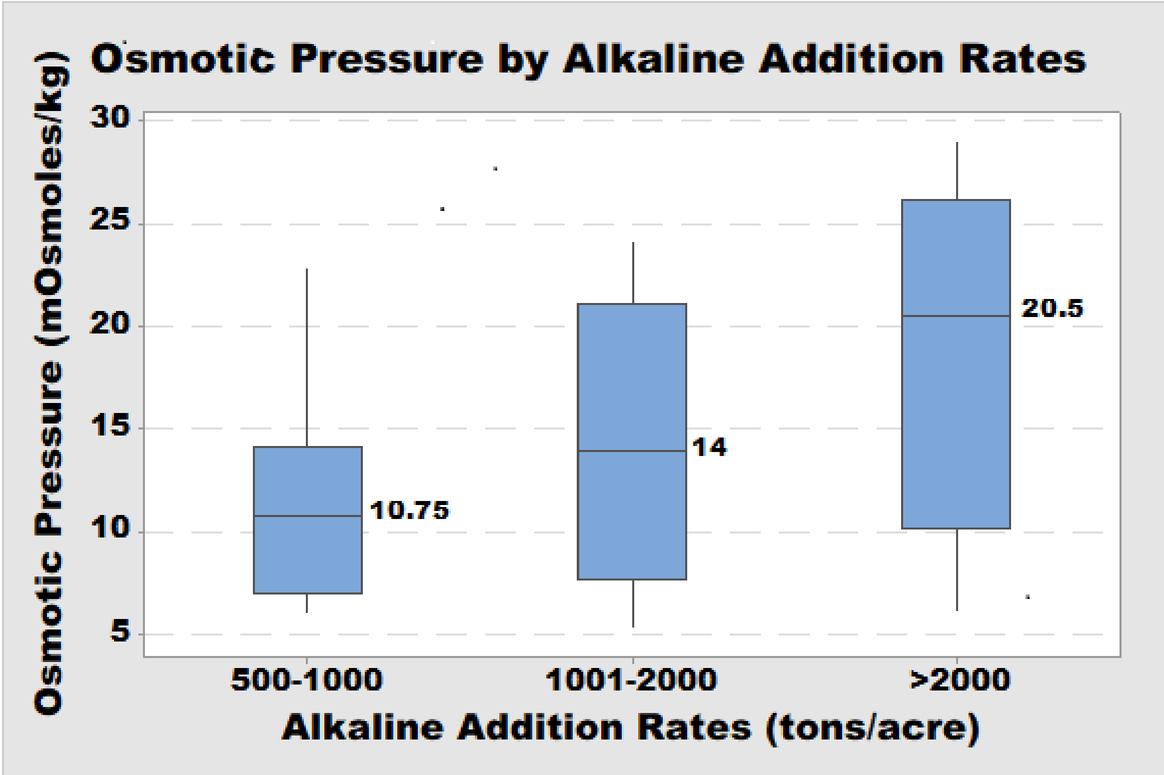

Figure 7. Box plots showing OP for three classes of alkaline addition rates. The blue box is bounded by upper and lower quartile values while the vertical line shows the entire range. The horizontal line indicates median value.

EPA frequently requests that OP be listed as a monitor and report parameter if there is an expectation that one half of the permit limit, or 25 mOsm/kg, may be exceeded. Only four sites had OP exceeding 25 mOsm/kg, with the lowest alkaline addition rate of 1891 tons per acre. A reasonable threshold to require monitoring and reporting for OP would be approximately 2000 tons per acre.

The similarity between the postmining water quality characteristics noted in this study and Brady et.al. (1994) suggest that imported carbonate material acts very similar to naturally-occurring carbonate. As with the Brady et.al. study of acid-base accounting, there is little correlation between sulfate concentration and alkaline addition rate (Figure 8) indicating that alkaline addition, at least at the typical application rate to achieve a NNP of 6, has little if any effect on reducing sulfate concentration by inhibiting pyrite oxidation. If anything, the data show a very weak trend of increasing sulfate with increasing alkaline addition. This is likely an artifact of how alkaline addition rates are calculated. The greater the sulfur content, the greater the alkaline addition needed to achieve a NNP of 6. Nonetheless, failure to add sufficient alkaline material to maintain an alkaline backfill environment could lead to extremely high sulfur contents if the site turns acid producing, owing to the lack of constraints on pyrite oxidation in an acidic environment.

Similarly, and perhaps surprisingly, postmining alkalinity (Figure 9) shows virtually no relationship to alkaline addition rates. This may be due to solubility constraints on alkalinity, which is influenced by CO_2 partial pressures, limiting the production of alkalinity. The Fran site, with an alkalinity of 1110 mg/l, is a notable exception, probably due to the very recent application of waste lime, which includes a fraction of hydrated lime that reacts very quickly.

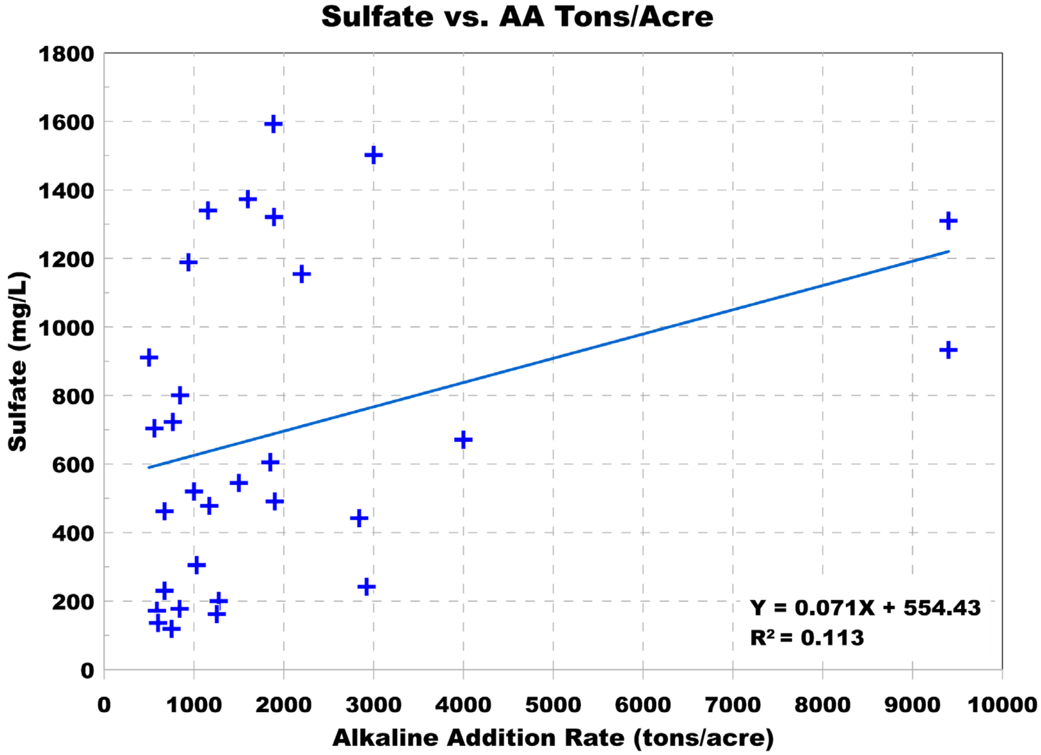

Figure 8. Postmining sulfate versus alkaline addition rate in tons per acre.

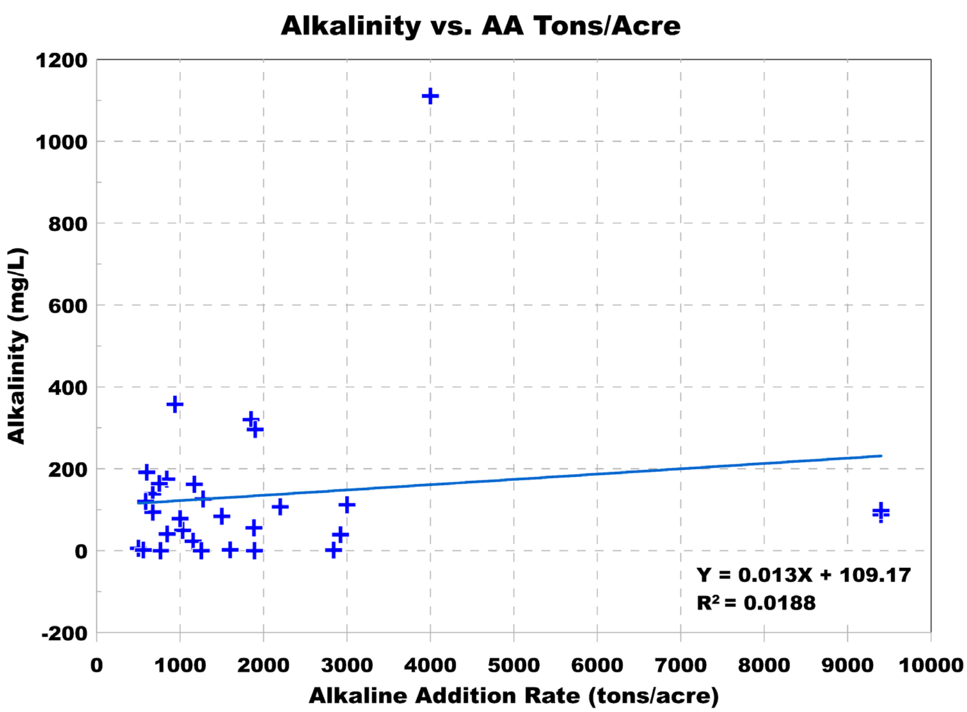

Figure 9. Postmining alkalinity versus alkaline addition rate in pounds per acre.

Conclusions

1. Alkaline addition at almost any typical mine applying alkaline material up to 4,000 tons/acre is unlikely to cause the osmotic pressure limit of 50 mOsm/kg to be exceeded.

2. Alkaline addition rates above 2,000 tons per acre may cause post-alkaline addition water quality to exceed 25 mOsm/kg and should be considered for monitor and report effluent limits.

3. Alkaline addition using an application rate sufficient to achieve a net neutralization potential (NNP) of 6 or greater (12 or greater without thresholds) has been very successful in assuring alkaline drainage. Of 21 sites, 20 (95%) produced alkaline drainage.

4. Alkaline addition cannot be depended on to assure that postmining water quality will meet applicable iron or manganese standards and does not appear to have any significant effect on reducing postmining manganese levels. Of the entire population of 44 sites, 19 (43%) had indicators of possible metals exceedances which usually (16 out of 19 times) included manganese.

5. Alkaline addition sites with modest application rates between 201 and 500 tons per acre (200 and below has been considered best management practice) have produced alkaline drainage without exceeding §87.102 instantaneous maximum (or met Subchapter F loading standards) except for one site where all of the alkaline material was placed on the pit floor and three sites where the application rate was calculated to achieve a NNP less than 3. Raising the threshold for best management practice alkaline addition from 200 tons/acre to 500/tons per acre should be considered, provided that the application rate is based on a NNP of 6 or higher and done according to established guidance.

6. Alkaline addition sites where the target NNP was less than 6 had a significant (25%) likelihood of producing acidic drainage, regardless of application rate and method of application. Of 16 sites with a target NNP less than 6, 4 produced acidic drainage, despite of application rates as high as 2840 tons per acre.

7. Ground-water monitoring at many alkaline addition areas was insufficient to determine the impact that alkaline addition was having on backfill water quality, leading to numerous sites being excluded from the study. Most stream monitoring points, springs and seeps are not adequately connected to the backfill area to serve as effective monitoring points. Although the current technical guidance allows for alternatives to monitoring wells, many of the alternates identified in the permit application were inadequate. Continued advancement of our knowledge and confidence in alkaline addition is dependent on adequate monitoring of impacts to water quality.

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