The natural logarithms of each of these parameters were also included in the correlation analysis to determine if any non-linear relationships existed. (Note: Numerous other transformations were also employed to investigate the nature of these relationships but were not fruitful and were therefore omitted.)

An analysis of correlation matrix r-values revealed that the natural log of the residence time (ln(t)) explained a significant amount of variation in net alkalinity generation (r=0.7414) (Figure 3.7). This indicates that the most rapid gain in alkalinity generation occurs within the first several hours of contact. Any additional residence time yields an ever-decreasing gain in alkalinity. This agrees with the decreasing solubility of the limestone as the water reaches saturation with respect to calcite (Hedin and Watzlaf, 1994). The non-Mn acidity proved to be a stronger indicator of alkalinity generation than total acidity, increasing the r-value from 0.5632 to 0.6919 (Figure 3.8). Total iron showed strong positive linear and logarithmic trends with r-values of 0.7357 and 0.7634 respectively (Figure 3.9). These findings indicate that residence time and influent water quality affect SAPS performance with respect to net alkalinity generation.
Figure 3.7 Relationship between residence time and net alkalinity (CaCO$_3$ equivalent) generation for the eight SAPS systems. $n = 135$
Figure 3.8 Relationship between non-Mn acidity and net alkalinity generation for the eight SAPS systems. Values represent CaCO$_3$ equivalent. $n = 135$
Figure 3.9 Relationship between influent iron concentration and net alkalinity generation for the eight SAPS systems. Net alkalinity values represent CaCO$_3$ equivalent. $n = 135$
A secondary analysis of the variables was performed to determine if there were any combined effects on net alkalinity generation. All of the variables were modeled against net alkalinity generation using a multivariate regression procedure. Potential variables were eliminated if they were found to be highly correlated (>0.9) with another model variable to reduce the problem of multicollinearity (Hinkelmann, 1999). The final variables and their coefficients were determined by using a least squares solution to the general linear regression model. This resulted in a model that proved to be significant (p>0.001) and more descriptive than any single variable with an $R^2 = 0.7852$ (Eq. 3.3). This model was then adjusted by multiplying

\[
\text{Net Alkalinity (mg/l as CaCO}_3\text{)} = 35.05 \ln(t_r) + 0.60 \text{Fe} + 0.55 \text{Non-Mn Acidity} - 48.49
\]

(3.3)

the equation by a factor of 1.275 to produce a slope of 1 for regression of the observed versus predicted values (Figure 3.10). This produced the model:

\[
\text{Net Alkalinity (mg/l as CaCO}_3\text{)} = 44.69 \ln(t_r) + 0.77 \text{Fe} + 0.70 \text{Non-Mn Acidity} - 61.82
\]

(3.4)

**Model Calibration**

In order to improve the accuracy of this model, independent sets of data were obtained from SAPS researchers in West Virginia and Pennsylvania. All of these systems met the same guidelines for inclusion as those in the study. Individual sampling events were excluded based on the criteria used in the model development. This process produced a total of 45 sampling events from five different SAPS that were suitable for use in the model calibration process. The average water quality
Figure 3.10  Relationship between observed and predicted values for the preliminary SAPS net alkalinity generation model using the model data set. Values represent CaCO₃ equivalent. n=135
parameters for these five systems are outlined in table 3.5. These systems were also evaluated to determine how they related to the SAPS systems used to develop the model. Figures 3.11 through 3.14 show the average values for all model parameters for both the model and calibration data sets. The residence times and non-Mn acidities were distributed with respect to the model data. Influent iron and net alkalinity generation tended to be higher than the majority of the systems in the model but still constituted a good overall distribution. More importantly, however, these systems also represented some of the more serious AMD situations that are common to northern Appalachia. This was deemed to be beneficial to the calibration process as it would better reflect the range of discharges that SAPS are designed to treat.

The data were initially analyzed to determine if net alkalinity generation responded to residence time and water quality in a similar manner to the SAPS in the study. This was done by developing a Pearson’s correlation coefficient matrix in the same manner as before (Table 3.6). Most relationships proved to be markedly similar in both degree and direction to those of the model data set. As before, log residence time proved to be a strong indicator of net alkalinity generation with an r-value of 0.7204 (Figure 3.15). Non-Mn acidity was also a better indicator than total acidity with r-values of 0.6712 and 0.6626 respectively (Figure 3.16). Total iron concentration exhibited a strong linear trend (r=0.7085) and much weaker logarithmic trend (r=0.5453) (Figure 3.17). This analysis suggested that both sets of SAPS systems responded to influent water quality in a similar manner.

The model was calibrated using the new data set through an iterative process of parameter adjustment that maximized the model R-squared values for each of the set of data independently. This was done by developing a third data set that