# Chapter VI

## Remediation study of mine waters/acid leachates by using nano-sized limestone

## 6.0 Introduction

The coal mining activities can largely determine the socio-economic status of a country although the other industrial development is also important for the development of a country. Besides this unavoidable importance of coal utilization, its negative impact on the environment cannot be ignored. The major problem arises from coal mining activities especially in the Ledo open cast mining in the Makum coal field of Assam (India) producing AMD. The acidic water produced in coal mining is responsible for several environmental affects, mainly the dissolution of potentially hazardous elements (PHEs) present in the coal which can act as a major contaminant for nearby water resources. The PHEs are more susceptible to low pH for their dissolution. So, high acidity of AMD is the major contributing factor for contamination of different metals and non -metals with water. These elements can enter the body of human beings and animals through drinking water and it can produce threat to aquatic life system. Thus, it is necessary to minimize the contact of AMD with other water bodies through proper treatment.

The mine drainage may remain for decades in the mine site and nearby areas by imparting severe environmental effects (Khayrulina et al., 2016). For instance, in United Kingdom alone it is predicted that presently almost six percent of total surface water bodies are adversely affected by acid mine drainage resulting from metalliferous mines (Mayes et al., 2009). In the same way, in USA it is expected that more than 19,300 km of rivers and above180,000 acres of lakes and reservoirs have been spoiled by AMD ( Kleimann et al., 1989). Thus, inventive mitigation approaches should be implemented to neutralize the acidity and inhibit the mobilization of trace and hazardous elements in AMD. Though most of the countries have taken different remediation processes, it is often not sufficient for controlling the degradation of the environmental quality in these mine sites. The Brazilian actions taken to solve acidity, include the application of a the calcination of calcareous rock material containing high CaO and MgO contents and disposal of mine tailings between compact soil layers by decreasing its exposure to atmospheric oxygen and water (Campaner et al., 2014). The GYP-CIX method is used in South Africa in which well-known cation-anion exchange resins are used, which exchanges cations ($Ca^{2+}$) and anions($SO_4^{2-}$) AMD with $H^+$ and $OH^-$ ions from AMD (Bowell, 2004).

In the process of regeneration, lime and sulphuric acid are used as alkali and an acid respectively due to their low cost. Another method used in South Africa is the flushing where the mine water is drained quickly from spoil heaps before accumulation to high levels can occur. Nano particle-assisted remediation is a new and emerging technique and was recently used by Das (2018) where zero valent Iron (ZVI) nano particles for the treatment of soil and water loaded with heavy metal rich AMD was used. The use of nano ZVI is not very eco-friendly due to the small size, a large surface area and high mobility; it can easily spread into the environment. Thus, in the present study a new concept of a nano remediation process, by using nano limestone (although it is laboratory based) for AMD treatment, has been introduced which may have minimum environmental effect.

## 6.1 Experimental sections

### 6.1.1 Samples

The reference mine water (AMD) was collected from Ledo colliery in a plastic gallon by using standard ASTM method. The collected sample was filtered with Whatmann 41 filter paper and then used for determination of physicochemical parameters, pH, TDS, and EC by using a EUTECH PC700 pH/EC/TDS meter. The determination of these parameters of the mine water sample is necessary, because from these values it is possible to calculate of amount of limestone needed for complete neutralization (pH7) of AMD. After determination the pH, TDS, and EC of the mine water was found to be 3.0,

### 6.1.2 Remedial method

A preliminary remediation experiment for the neutralization of a representative AMD sample (LW-15D) from Ledo colliery was done by using Meghalaya limestone. Four different mesh sizes, namely 0.296 mm, 0.420 mm 3.180 mm and □ 3.180 mm of limestone were used in this experiment and these were packed in four numbers of columns of same sizes (with volume capacity 25 mL). Each of the columns was filled with equal amounts of limestone (16 g). The representative mine water, having pH value 3.30 was poured slowly in an equal amount into the columns and after pouring a definite amount, pH, TDS and EC of the mine waters were determined. The limestone solution became neutral after passing a definite volume of mine water through the columns and then these were packed with new lime stone. The total amount of limestone used in each column for neutralization was recorded. Finally, the volumes of mine water needed in each column for complete neutralization (up to pH 6.5-7) were collected and the final pH, TDS, and EC of treated mine waters from each column were determined by pH/EC /TDS meter. The simple experimental method used for lab-scale remediation process is depicted in Figure 6.1.

Figure 6.1: Photograph of the lab-scale AMD remediation process

## 6.2 Lab-scale remediation study for neutralization of AMD by nano-limestone

For complete neutralization and minimization of concentrations of potentially hazardous elements in AMD a laboratory-based remediation experiment has been carried out by using limestone which can neutralize the acidity of AMD to a major extent. The volume of mine water utilized to get neutral mine water in all columns were collected frequently after a specific duration to determine the pH, TDS, and EC at different intervals. Moreover, the amount of lime stone used in the columns for complete neutralization was also recorded .The Table 6.1, Table 6.2, and Table 6.3 show that after passing 50 mL of mine water through the columns with 0.296 mm, 0.420 mm, 3.180 mm and □3.180 mm limestone, the pH of the mine water was found to be 3.50, 3.80, 6.70, and 6.97 respectively. Accordingly, at this stage the mine water had TDS values 6.41, 2.30, 1.89, and 1.43 ppt and EC values 12.59, 8.80, 2.95 and 2.48 mscm$^{-1}$ respectively. After passing 100 mL of mine water through the columns having limestone of, it was found that the mine water became almost neutral. After recording these parameters, another 50 mL of mine water was passed through the columns with 0.296 mm and 0.420 mm limestone and the resulting water was used for analyzing pH, TDS, and EC and the values were found to be 3.62, and 4.0; 2.48 and 1.69 ppt, and 7.59 and 4.96 mscm$^{-1}$ respectively. After passing this amount of mine water, it was recorded that the pH, TDS, and EC values became constant even the volume of mine water to be passed was increased upto 150 mL. This means that these mesh sized (0.296 mm and 0.420 mm) limestone has the capability to minimize the pH of only 100 mL AMD water. Thus, the limestone used in the columns with 0.296 mm, 0.420 mm was changed with the same amount and size of new limestone and then 80 mL of treated mine water was passed through them. Then water was collected from the columns and again their pH, TDS, and EC were determined. The pH, TDS, and EC of water from column with 0.420 mm limestone were found to be 4.0, 1.65 ppt and 3.71mscm$^{-1}$ respectively. On the other hand, the water from the column with 0.296 mm limestone was recorded with pH, TDS, and EC values 7.31, 1.65 ppt, and 3.79 mscm$^{-1}$

respectively. Thus, after passing this volume the mine water through 0.296 mm sized limestone it was found that the water was almost neutral. So, another 70 ml of used mine water was passed through the column packed with 0.420 mm limestone and the pH, TDS, and EC values were found to be 6.79, 1.03 ppt, and 3.34 mscm$^{-1}$ respectively. Thus, from this experiment we can be revealed that the neutralization of AMD water is completely dependent on the size of limestone used. The larger the size of limestone, the faster will be the process of neutralization. Another major fact obtained from this remediation process is that apart from the neutralization, this process is also helpful for minimization of concentration of heavy metals which are normally dissolved in AMD. Moreover, the results of ICP-OES analysis of treated mine water confirms that the concentrations of most of the elements present in AMD were reduced after treatment with limestone. Table 6.1, Table 6.2, and Table 6.3 show the dependence of pH, TDS, and EC of mine water with the size of the limestone particles used. The data obtained for different physico-chemical parameters after treatment with different sizes of limestone, it was clear that these parameters were completely dependent on the size of the limestone used. Figure 6.2 shows the variation of concentration of some reference elements present in untreated AMD and in treated AMD which is shown by Table 6.4.

Table 6.1: Change in pH with volume of mine water during neutralization

| Sample | Initial pH | Size of limestone(mm) | pH after passing 50 ml AMD | pH after passing 100 ml AMD | pH after passing 150 ml AMD | pH after passing used 80 ml AMD through new lime stone | pH after passing treated 150 ml AMD through new lime stone | Total amount of limestone (g) |
|---|---|---|---|---|---|---|---|---|
| AMD water | 3.3 | 0.296 | 3.5 | 3.62 | 3.62 | 4 | 6.79 | 96 |
| | | 0.420 | 3.8 | 4 | 4 | 7.11 | 7.11 | 32 |
| | | 3.180 | 6.7 | 6.8 | 6.8 | 6.8 | 6.8 | 16 |
| | | > 3.180 | 6.97 | 7 | 7 | 7 | 7 | 16 |

Table 6.2: Change in TDS with volume of mine water during neutralization

| Sample | Initial TDS (ppt) | Size of limestone | TDS after passing 50 ml (ppt) | TDS after passing 100 ml (ppt) | TDS after passing 150 ml (ppt) | TDS after passing used 80 ml through new limestone (ppt) | TDS after passing used 150 ml through new lime stone (ppt) | Total amount of limestone (g ) |
|---|---|---|---|---|---|---|---|---|
| AMD water | 7.20 | 0.296 | 6.41 | 2.48 | 2.44 | 1.48 | 1.03 | 96 |
| | | 0.420 | 2.30 | 1.69 | 1.65 | 1.65 | 1.65 | 32 |
| | | 3.180 | 1.89 | 1.85 | 1.85 | 1.85 | 1.85 | 16 |
| | | □ 3.180 | 1.43 | 1.39 | 1.39 | 1.39 | 1.39 | 16 |

Table 6.3: Change in EC with volume of mine water during neutralization

| Sample | Initial EC mscm$^{-1}$ | Size of limestone(BS) | EC after passing 50 ml AMD (mscm$^{-1}$) | EC after passing 100 ml AMD (mscm$^{-1}$) | EC after passing 150 ml AMD (mscm$^{-1}$) | EC after passing used 80 ml AMD through new limestone (mscm$^{-1}$) | EC after passing treated 150 ml AMD through new lime stone (mscm$^{-1}$) | Total amount of limestone ( g ) |
|---|---|---|---|---|---|---|---|---|
| AMD water | 22.5 | 0.296 | 12.59 | 7.59 | 7.42 | 3.71 | 3.34 | 96 |
| | | 0.420 | 8.8 | 4.96 | 4.89 | 3.79 | 3.76 | 32 |
| | | 3.180 | 2.95 | 2.90 | 2.90 | 2.90 | 2.90 | 16 |
| | | □ 3.180 | 2.48 | 2.50 | 2.50 | 2.50 | 2.50 | 16 |

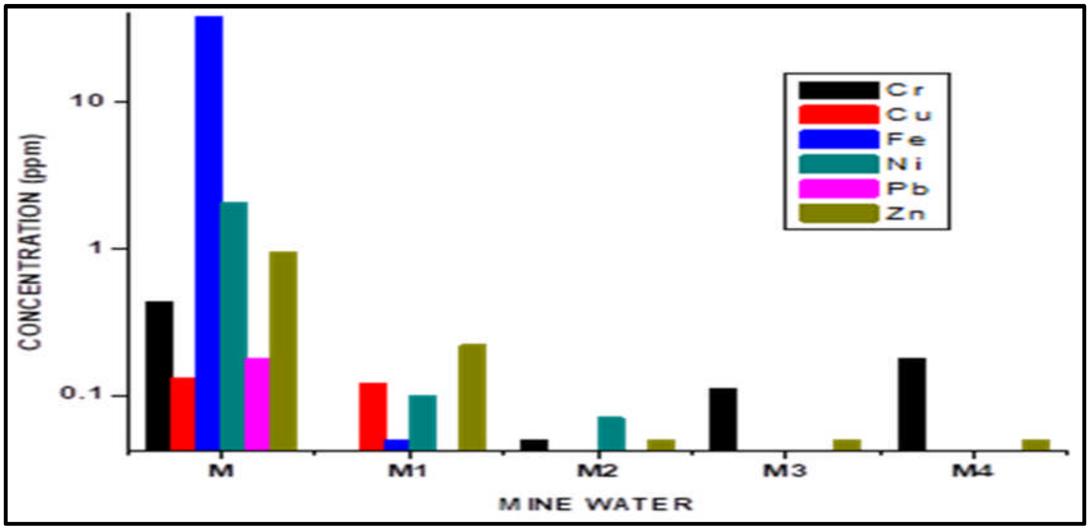

Figure 6.2: Variation of elemental concentration in treated AMD from untreated AMD

(Here, M: untreated mine water; M1, M2, M3, and M4: treated mine water)

Table 6.4: Percentage of elemental absorption in treated AMD

| Untreated AMD (M) | | Treated AMD | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Elements | Concentration (ppm) | Elements | M1 | | M2 | | M3 | | M4 | |
| | | | Concentration (ppm) | Amount of absorption (%) | Concentration (ppm) | Amount of absorption (%) | Concentration (ppm) | Amount of absorption (%) | Concentration(ppm) | Amount of absorption (%) |
| Cr | 0.43 | Cr | 0.01 | 97.67 | 0.05 | 88.37 | 0.11 | 74.41 | 0.18 | 58.14 |
| Cu | 0.13 | Cu | 0.12 | 7.69 | 0.03 | 76.92 | 0.01 | 92.3 | 0 | 100 |
| Fe | 39.01 | Fe | 0.05 | 99.87 | 0.02 | 99.94 | 0.01 | 99.97 | 0 | 100 |
| Ni | 2.06 | Ni | 0.1 | 95.15 | 0.07 | 96.6 | 0.04 | 98.06 | 0.02 | 99.03 |
| Pb | 0.18 | Pb | 0.01 | 94.44 | 0.01 | 94.44 | 0.01 | 94.44 | 0.01 | 94.44 |
| Zn | 0.96 | Zn | 0.22 | 77.08 | 0.05 | 94.79 | 0.05 | 94.79 | 0.05 | 94.79 |

From Table 6.4, it is clear that with an increase in size of limestone used in the column, the percentage of absorption of elements was increased. In contrast, the amount of absorption of Cr decreased with increase of size of limestone which is reflected in Figure 6.3.

In case of the elements Cu, Fe, and Ni, the removal was almost completed when passed through limestone with particle size more than 1/8 screen fraction (Table 6.4). The percentages of absorption of Cr in the columns with limestone with sizes 0.296 mm (M1), 0.420 mm (M2), 3.180 mm (M3) and □3.180 mm (M4) were found to be 97.67, 88.37, 74.41, and 58.14% respectively. Thus, for substantial removal of Cr from mine water, a limestone with minimum particle size of is preferable.

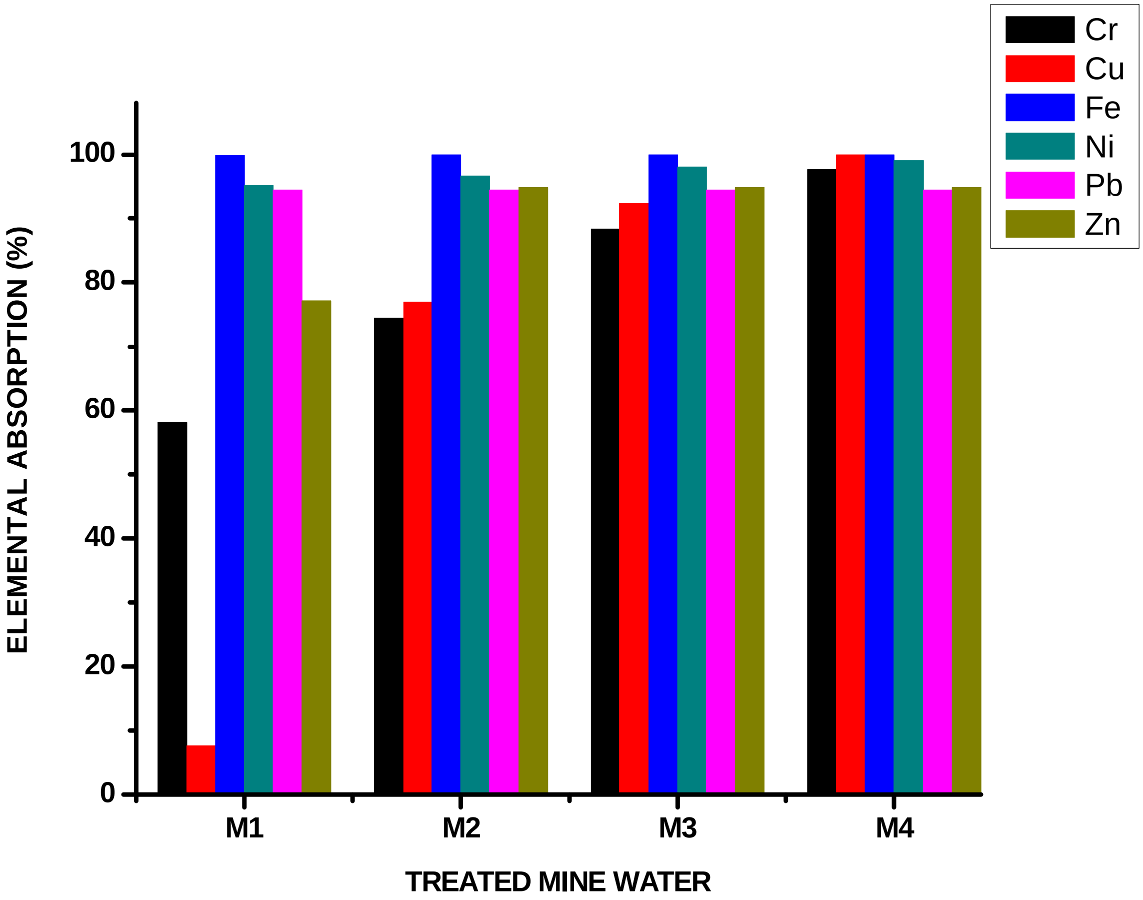

Figure 6.3: Percentage of absorption of elements in treated AMD

From HR-TEM analysis of limestone, it is confirmed that some fraction of Meghalaya limestone is composed of nano sized particles **(**Figure 6.4**).** Possibly for the presence of nano limestone particle, the percentage of absorption of Cr was highest in lowest sized limestone (0.296 mm).

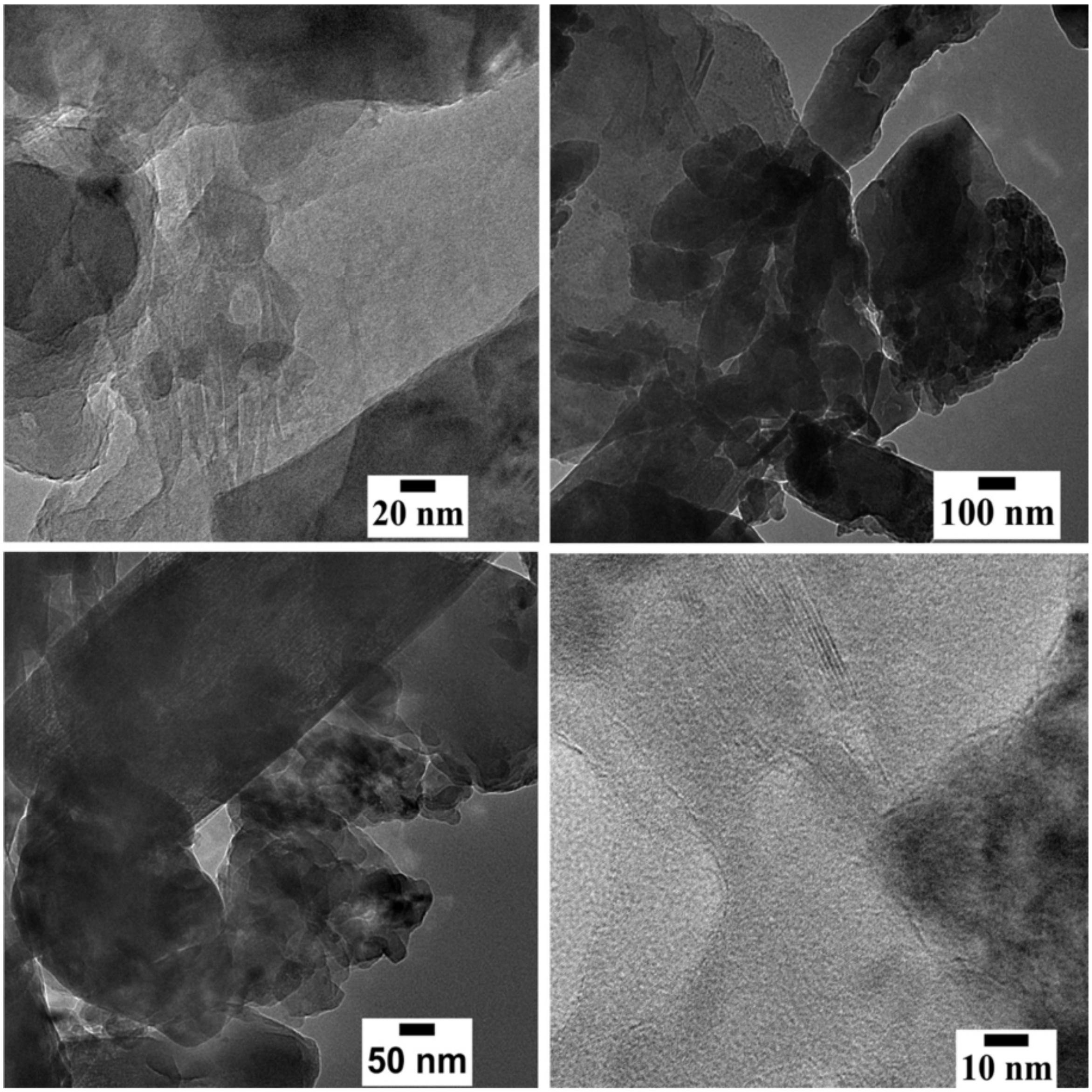

Figure 6.4: HR-TEM image of limestone showing the nano particles/structure

Moreover, the XRD analysis of the limestone used in the remediation process indicates the presence of most of the minerals found in coal **(**Figure 6.5). Thus by using this simple process for the treatment of acid mine drainage, a number of minerals which consist of different elements can be removed.

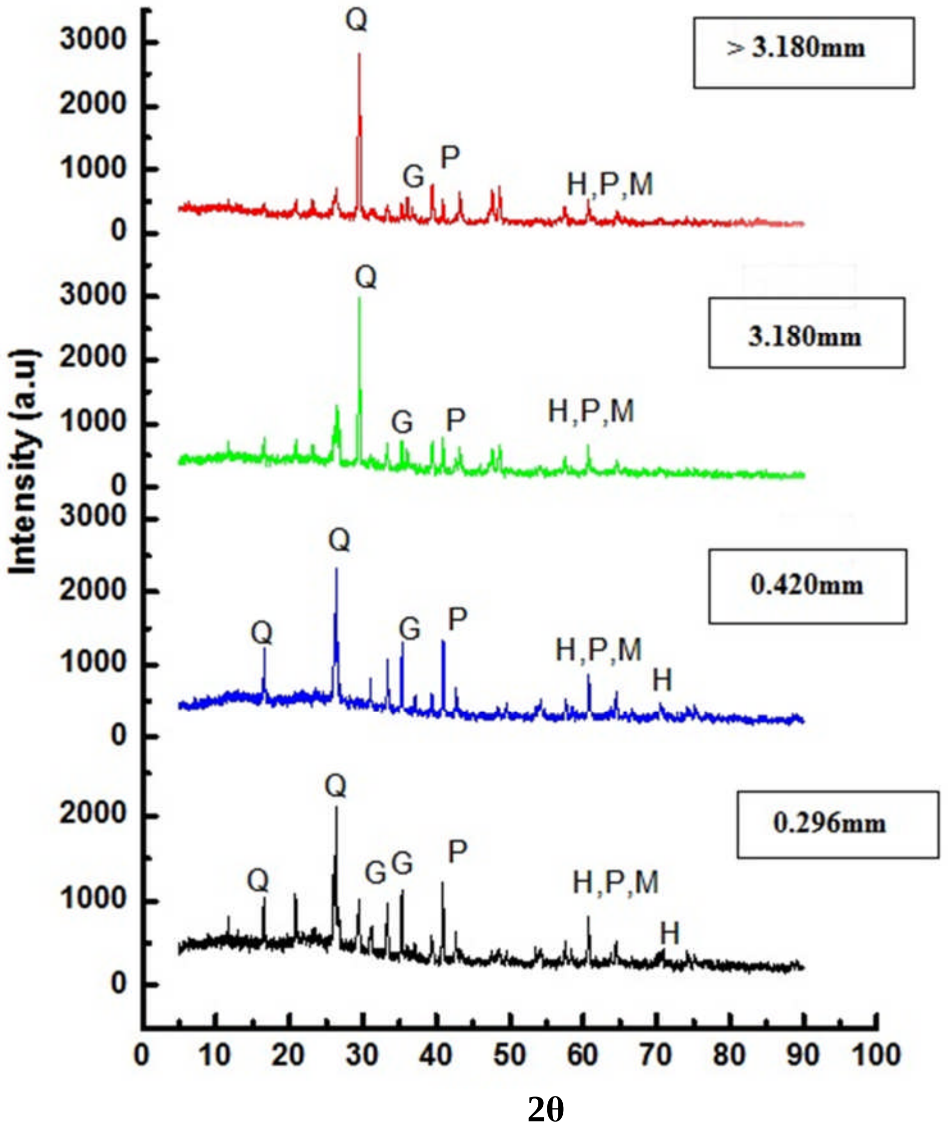

Figure 6.5: XRD graph of limestone used for remediation of AMD

(Q: Quartz; P: Pyrite; H: Hematite; G: Gypsum; M: Marcasite)

Since limestone is cheap, easy to handle and it offers an advantage for using as an effective media for neutralization and minimization of heavy metal contamination from AMD. Limestone increases the pH of AMD by consuming $H^+$ ions and increasing the bicarbonate concentrations (Younger et al., 2002).The usage of limestone for the treatment of acid mine drainage is based on the neutralization effect of Calcium or magnesium carbonates (Camila et al., 2013). Moreover, calcium carbonate used in the process can restrict the kinetics of pyrite oxidation, and even prevent the oxidation process (Caruccio and Geidel, 1996). Evangelou (1995) established that iron hydroxides can precipitate on the surface of pyrite minerals by decreasing the oxidation kinetics. In Brazil, Soares et al. (2006) estimated the effect of calcium and magnesium carbonates on controlling the acid mine drainage through neutralization as well as by decreasing metal mobilization in AMD generated from coal mine overburden**.**

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