# CHAPTER 4
# Leaching Studies

## 4.1 Introduction

The leaching process is defined as the dissolution of soluble constituents of solid material (like solid waste, soil, fly ash or any dumped waste material) by a liquid through percolation inside the solid medium. The liquid available in the dumped waste material, rainwater, surface runoff, or groundwater can act as percolating fluid in the leaching process. The final liquid extract releasing from the solid face is called leachate. The dissolution extent of solid media constituents is varying with the material and environmental condition of the location along with the duration of leaching. Evaluation of leaching will give a fair idea of the suitability of a waste to dump/fill at a specific location. Ecosystem near the solid waste landfill sites is prone to affect by the quality and quantity of the disposed wastes. A schematic layout of the effects on the surrounding environment due to waste disposal is shown in Fig. 4.1. There is a possible contamination of air directly from the waste itself. The runoff from the disposal site of the waste may go directly into the source of surface water or through surface soil and pollute the soil and surface water bodies. The contaminated water coming from the dumping sites of the waste may infiltrate through surface water bodies to groundwater and contaminate it. Through leaching, it may penetrate to deep soil strata from surface/sub-surface soil and intermixed with groundwater through dispersion and diffusion.

Different methods have been developed by the researchers to study the leaching phenomenon. The laboratory leaching tests are conducted to serve the following objectives:

A. Different leachable constituent of solid mass can be identified when it come in contact with leachant fluid.

B. Assess whether dumping wastes are hazardous or nonhazardous after comparing leachate characteristics with the recommended guidelines.

C. Examine how the manufacturing process of a material affects the characteristics of wastes and leachate.

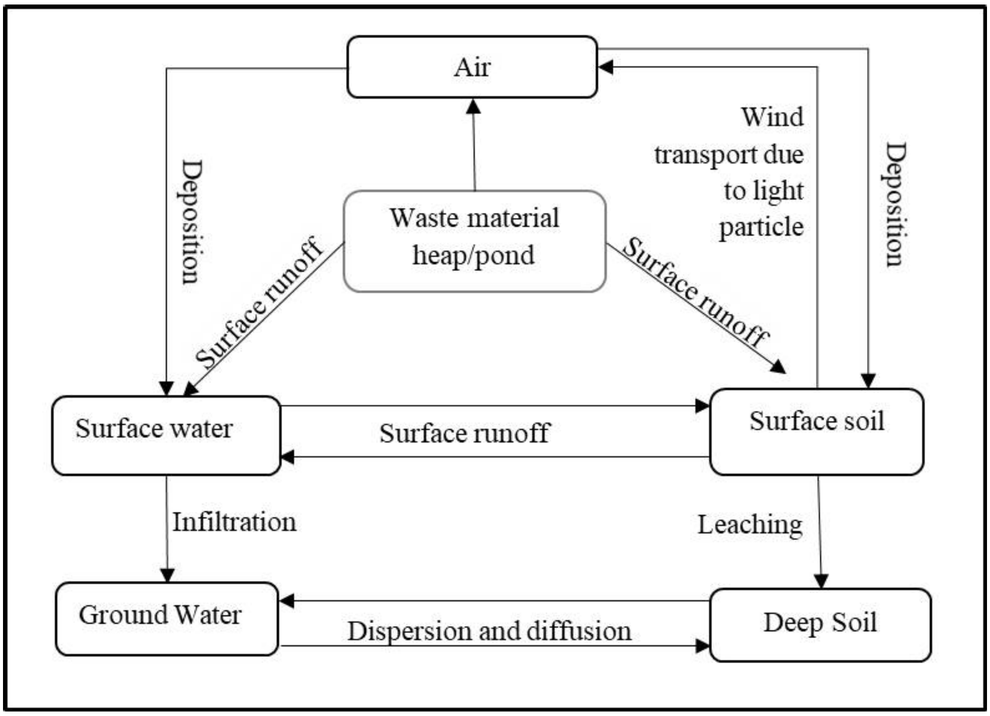


**Fig 4.1** The movement of waste material and liquid in the environment (Parisara-ENVIS, 2007)

D. Evaluate the effectiveness of the waste treatment process.

E. Design an effective method to treat leachate by characterizing its property.

F. Assess the effect of leaching for a given time on groundwater and modeling of groundwater subsequently.

G. Determine the value of different coefficients and parameters associated with transport phenomenon and modeling.

H. Assess environmental impact potential due to the disposal of specific wastes.

### 4.2 Classification of Leaching Tests

Based on the purpose, leaching tests methods can be broadly classified into three major parts (Environment Canada, 1990):

A. Leaching tests performed to replicate a precise environmental condition (like TCLP for acidic rain).

B. Tests used to extract specific chemicals from the material.

C. Procedure to identify basic leaching parameters.

Many researchers have studied the replication of leaching in actual environmental condition and suggest different methods of leaching to evaluate them in a laboratory environment.

Based on the characteristics of leachate, the leaching method may be static extraction tests (single addition) or is a dynamic test. To serve different proposes, researchers suggest various leaching tests. Many different assumptions are considered while performing leaching tests, are detailed in leaching environmental assessment framework (LEAF) test methods EPA/600/R-10/170, November 2010. Following are the aspects, which influence the solubility of leaching media:

A. pH is an essential parameter to regulate the solubility.

B. Effect on complexing agents in the dissolved phase will intensify the dissolution.

C. The oxidation-reduction potential very much influences solubility.

One stage leaching is most simple of all leaching tests. The optimum time is devoted in such a way so that the correct establishment of chemical equilibrium is achieved. The major hurdle of this is non-availability of accurate data, especially in context to temporal variation. The column leaching tests can provide a proper solution to such problems.

## 4.3 Material and Methods for the Laboratory Leaching Test

The pollution potential of fly ash and its properties are directly dependent on the mineralogy of parent coal (Scheetz and Earle, 1998). It has been observed that the concentration of trace elements in fly ash is higher than about 4–10 times of that in the parent coal because there is a loss of carbon in the form of carbon dioxide during the combustion of coal (Ugurlu, 2004). These trace elements are accumulated mainly owing to evaporation and condensation processes associated with fly ash under different operating conditions. They are vulnerable to mobilization and leaching when they meet leaching media, like rain or other aqueous solutions, especially in landfills and dumping sites (Akar et al., 2012; Ugurlu, 2004).

In this chapter, the immobilization potential of FA and CT are evaluated. To find out the leaching potential or adsorption behavior, batch and column leaching tests are performed, so that the actual environment condition can be replicated. The samples of FA were collected from the disposal site (29°10'31.371" N and 73°59'21.066" E) from Suratgarh Super Thermal Power Plant with the capacity of 1500 MW located near Suratgarh, district Sri Ganganagar, Rajasthan, India. The plant has produced about 169.25 megatons of coal FA from the combustion of 509.46 megatons of coal in the year 2016-17. Two types of samples have been collected to analyze mobility aspects of trace elements in fly ash under different environmental scenarios: (i) fresh fly ash sample collected just before its disposal at the dumping site (i.e., FA-1) and, (ii) weathered fly ash sample collected from the dumping site after 30 days of its disposal (i.e., FA-2). These samples were collected in the airtight containers to avoid losses. The particle size distribution of these samples varies from 0.002 mm to 0.075 mm, which is nearly identical, as reported by Akar et al. 2012. The CT samples were taken from copper tailings pond near Khetri Copper Complex, Hindustan Copper Limited (HCL) district Jhunjhunu, Rajasthan, India (27° 49' 59" N, 75° 46' 0" E). More details of these sampling sites are already discussed in Chapter 3.

Both FA and CT samples have been stored in an airtight container, and as they were in uniform powder form, hence no further milling is required. The average specific gravity of samples was measured as 2.1 and 3.2, respectively for FA and CT. In the laboratory, preserved fly ash samples were oven-dried and homogenized. The pH of each sample is measured with the 20 L/S ratio mixture after shaking them for 5 minutes.

For the elemental analysis, the samples were pretreated by fusion with lithium metaborate ($LiBO_2$) and the elements recovered in the aqueous solution were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The morphology of the samples was also examined using a Field Emission Gun Scanning Electron Microscope (FEG-SEM, JSM-7600F).

Elemental analyses and FEG-SEM analyses were carried out at the Sophisticated Analytical Instrument Facility, Indian Institutes of Technology (SAIF-IIT), Bombay.

To study the actual quality of groundwater near dumping sites, water samples are collected near disposal sites of both FA and CT. Seven groundwater samples have been taken from hand pump fitted bore wells located nearby (from 500 m to 12 km from FA sampling location) of the selected FA dumpsite. Ten water samples were also collected from different locations nearby of the CT pond. The samples have been preserved with nitric acid (pH <2) before performing the analysis to minimize the precipitation, microbial degradation, and adsorption at the container wall. Trace element analysis has been done by inductively coupled plasma mass spectrometry (ICP-MS) method using PerkinElmer SCIEX ELAN DRCe (detection limit up to ppb level) instrument available at Wadia Institute of Himalayan Geology, Dehra Dun, Uttarakhand, India.

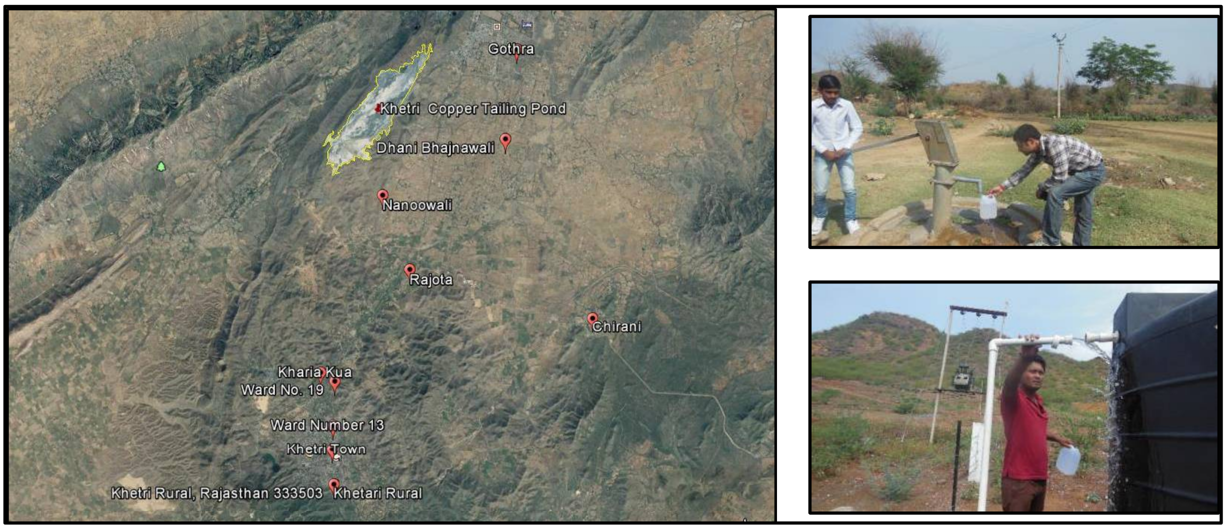


**Fig. 4.2** Collection of groundwater samples near Khetri Copper Lailing pond, Khetri

### 4.3.1 Batch leaching test

Two different prescribed leaching methods have been used to evaluate leaching characteristics of fly ash under different environmental situations:

### *A. Toxicity Characteristic Leaching Procedure (US: EPA method 1311, 1992)*

The leaching behavior of fly ash is examined using the TCLP test as per US EPA Resource Conservation and Recovery Act under acidic medium (US EPA Test Method 1311 1992). As per the TCLP protocol, glacial acidic acid (diluted to pH 2.88) has been used as the main leachant. Fly ash and extraction fluid (with L/S ratio 20) are poured in 300 ml bottles which are first cleaned with nitric acid. The horizontal shaking was done for 18 hours at 180 rpm and 25°C temperature. The similar procedure is followed for the combined TCLP batch experiment with different proportions of FA and CT. The details of mix proportion for batch leaching of FA and combined batch leaching of (FA and CT) are detailed in Appendix A.

### *B. Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM D39 87-85)*

This leaching method works effectively to evaluate inorganic extraction of solid waste. In this method, distilled water was used as a leachant, in 300 ml bottles (nitric acid cleaned) with L/S ratio 20. The shaking was done at 180 rpm and 25°C temperature for 18 hours to replicate normal environmental condition. The batch tests were also carried out with other L/S ratio values of 5, 10 and 50 for both types of leachants (pH 2.88 and 7) to find out the effect of different natural conditions. The fly ash samples were taken into nitric acid-cleaned 300 ml volume reagent bottles, and 100 ml of extraction fluid was added accordingly. Each batch test was conducted in duplicate. After agitation on the shaker for 18 hours, the mixture was allowed to settle for 5 minutes, and then the aqueous phase was separated by decantation, followed by filtration. The pH of the leachates was determined immediately just after the collection of the samples (as shown in Appendix A) with respect to the different L/S ratio. The leachates samples were stored in properly labeled airtight sample bottles after acidifying them with nitric acid (pH < 2). The similar procedure is followed for the combined ASTM batch experiment of FA and CT. The details of mix proportion for batch leaching of FA and combined batch leaching of (FA and CT) are detailed in Appendix A. Toxicity Characteristic Leaching Procedure (TCLP-1311) and Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM D3987-85) are the commonly used procedures, which are performed to determine short-term solubility characteristics. To overcome this, the dynamic leaching (column) tests serve as a highly attractive option which can monitor the metal release over longer durations and also can identify temporal variations in the contaminant concentrations during the course of its transport through the waste.

**Fig. 4.3** Batch leaching test performed in the laboratory

### 4.3.2 Column leaching test

The column experiments were conducted using an experimental setup that consisted of an extraction fluid reservoir, a peristaltic pump, and borosilicate glass columns. The columns were operated in an up-flow mode to prevent channeling and differential gravity flow effects between leachate and groundwater. Three different sets of column experiment were conducted for FA and CT. The glass column is filled with 21 cm equal height of FA and CT (bottom FA and top CT).

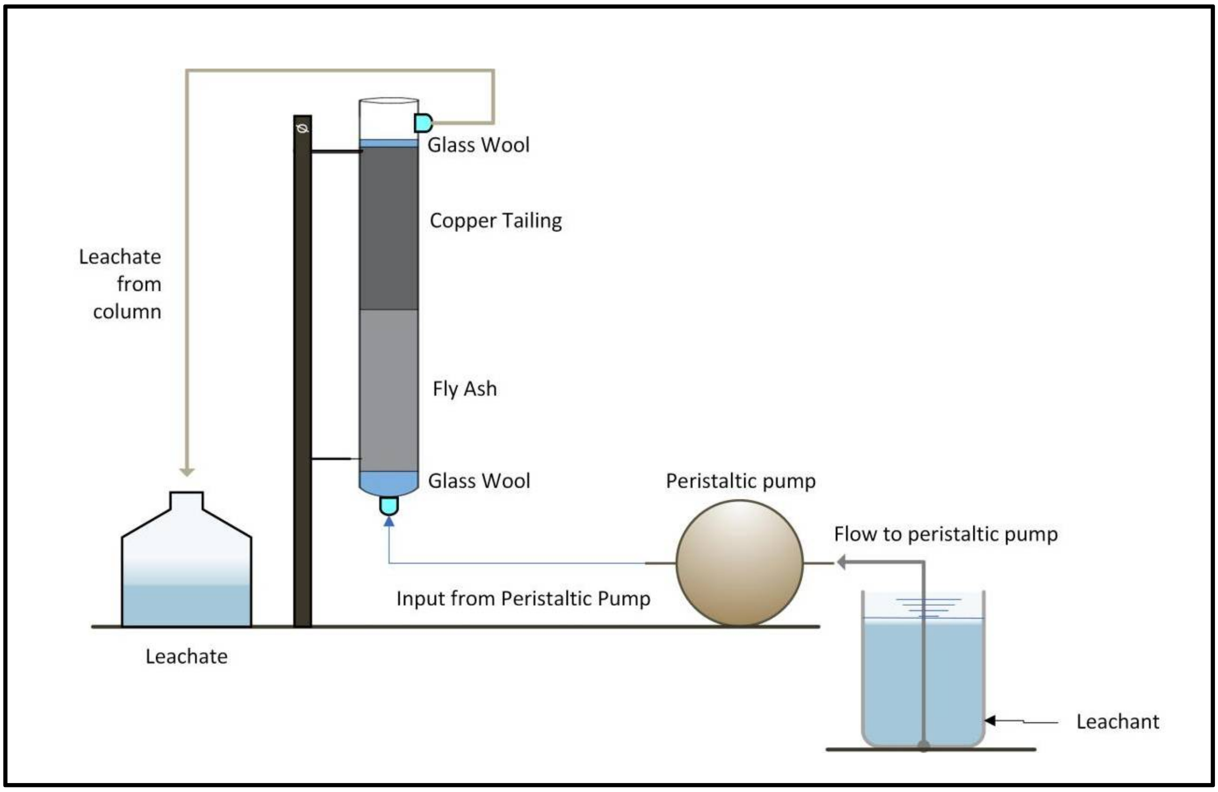


**Fig 4.4** Overview of the column leaching experiment set up

The bottom and top of material are covered with glass wool. In the three different sets of column experiment, extraction fluid was distilled water, acetic acid 0.01M (pH 2.88) and alkaline solution (0.0015M NaOH solution). The leachates were collected in cylindrical bottles for each set in a given time interval (initially after the continuous running of 16 hrs then after the interval of 8 hrs, 12 hrs, 18 hrs, 24 hrs, 24 hrs, 24 hrs and last after 24 hrs) and filtered and acidified to preserve before performing the analysis. All the samples were preserved in airtight bottles after lowering the pH nearly two by adding nitric acid.

**Fig 4.5** Experimental setup in the laboratory

## 4.4 Results

### 4.4.1 ICP AES results of FA-1 and FA-2

The ICP-AES test results, for both the FA samples, have been plotted on a semi-log graph as shown in Fig. 4.6 with the logarithmic scale on the horizontal axis (abscissa). The result of ICP-AES reveals the presence of elements Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Sr, Cd, Ba, and Pb in samples, in which Mg, Al, Si, Ca, Ti, and Fe are predominant in both the samples, viz. FA-1 and FA-2. Si and Fe concentrations are higher in the case of weathered sample but Mg, Al, Ca, and Ti concentrations are decreasing with time from FA-1 to FA-2. Al and V concentrations in FA-1 and FA-2 are much higher than the prescribed limit as specified by the New Zealand landfill screening criteria for both Class A and Class B landfills classifications.

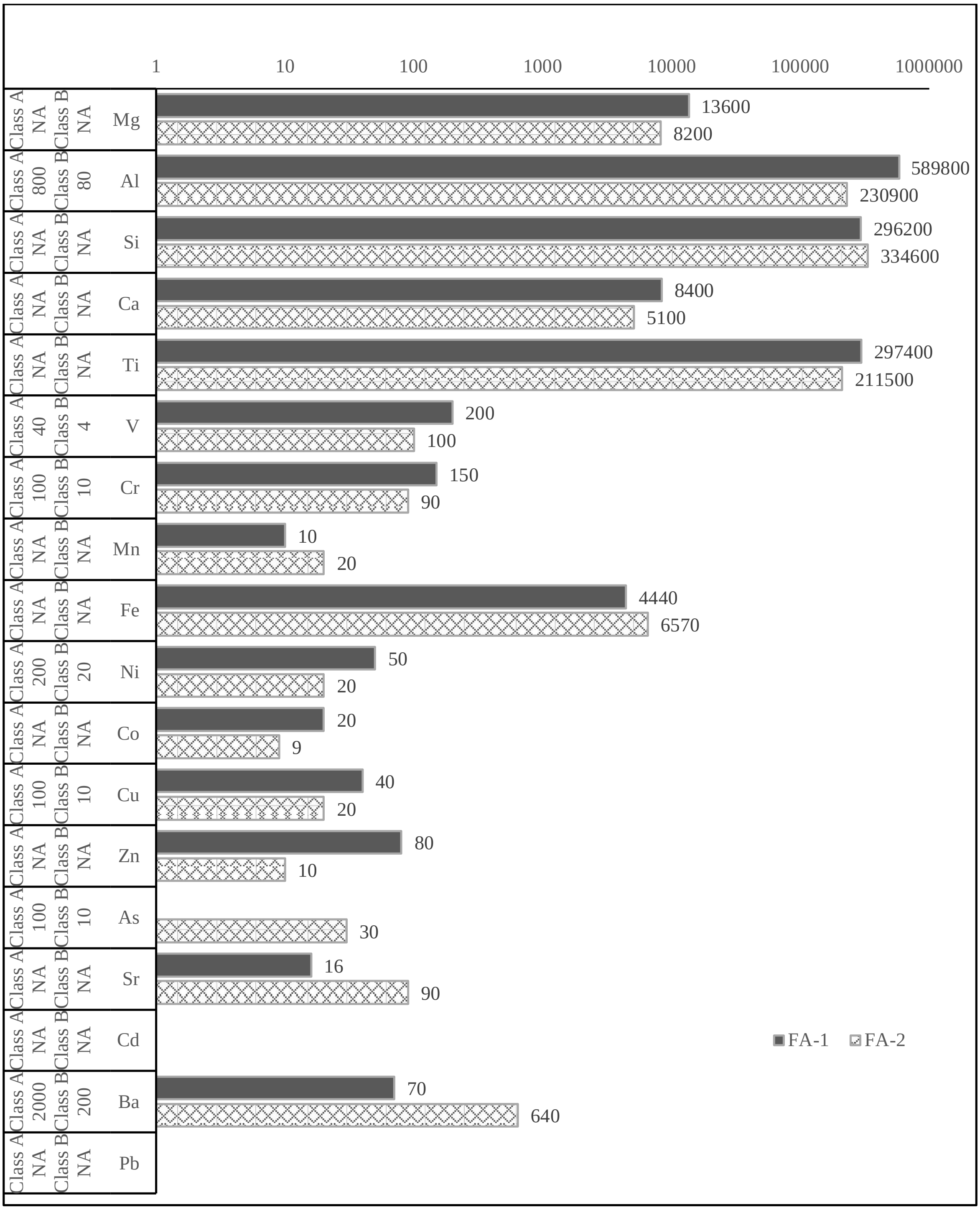


**Fig. 4.6** Concentration of elements in FA-1 and FA-2 along with waste acceptance criteria for Class A and Class B landfill (all values are in mg/kg) (x-axis plotted on a log scale to visualize the difference properly)

The value of Cr in FA-1 is greater than the prescribed standard limit for both Class A and Class B landfill criteria whereas its value in FA-2 samples are higher than the prescribed standard limit for Class B criteria. Similarly, As and Ba concentration values in FA-2 samples are greater than the prescribed standard limit for Class B criteria only. The value of Zn in FA-1 samples is four times higher than the prescribed limit under Class B criteria. Cu concentration in both FA-1 and FA-2 samples and Ni in FA-1 samples only exceeds the Class B screening criteria. The analytical results were compared with the standard specifications available in the literature, especially concerning the waste acceptance criteria for class A and class B landfill (MFENZG, 2004). Individual mineralogy of FA and CT are presented earlier in Chapter 3.

### 4.4.2 Batch leaching test results

The findings of Toxicity Characteristic Leaching Procedure (TCLP) and ASTM leaching tests for individual FA-1 and FA-2 samples are presented in Table 4.1. In this, the leachability of elements Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, Si, Sr, Ti, V and Zn have been compared with the prescribed regulatory value of TCLP by the United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) drinking water standards. There is a pH dependency on the leaching behaviour of fly ash, which has also been reported by many researchers (Singh et al., 2014; Izquierdo and Querol, 2012). It can be observed from Table 4.1 that the concentration of all selected elements in representative leachate samples using TCLP is higher than those obtained from ASTM. It can also be inferred that the pH value decreases with an increase in L/S ratio in case of both the leachate samples (i.e., FA-1 and FA-2) as shown in Fig. 4.7. It indicates that the fly ash imparts alkalinity to the leachate solution (Neupane et al. 2013). The concentration of all elements for both tests is much below the limits set under US EPA TCLP guidelines.

The concentration of Cd in the FA-1 samples by TCLP test has been found exactly equal to the WHO drinking water standard. Ca, Cu, Mg and Zn concentrations, in FA-1 and FA-2 samples, in both tests, are considerably below the WHO prescribed limits. The value of Pb is a little alarming in the case of FA-1 and FA-2 samples for both tests. In FA-2 samples, concentration of As, Ba and Se are within the prescribed WHO limit except ASTM results of Ba, but in FA-1 samples, the value of As is about 20-fold higher for both tests and Se concentration is slightly higher than WHO prescribed guidelines for both tests in FA-1 samples. The concentration of Ni is only higher than the permissible limit in TCLP test results, for FA-1 and FA-2 samples, which confirms its greater affinity for acidic leachant. Fe concentrations are much higher nearly six times and 44 times for TCLP test results in both FA-1 and FA-2 samples than WHO prescribed limits. In ASTM, Fe concentration is 3-fold higher for FA-2 and nearly equal in FA-1, signifies that leaching of Fe is also taking place significantly in the acidic medium. Leaching behavior of Mn is about 23 and 30 folds higher in TCLP results for FA-1 and FA-2 respectively and four-times higher in ASTM results of FA-1 and FA-2 samples. Except for FA-2 samples in ASTM result, Cr concentrations are higher than the permissible limits. The WHO permissible limit for Cr is 0.05 mg/L, which is nearly four times higher for FA-1 samples in TCLP and three times higher in ASTM results respectively and 0.02 mg/L higher in TCLP result for FA-2 samples.

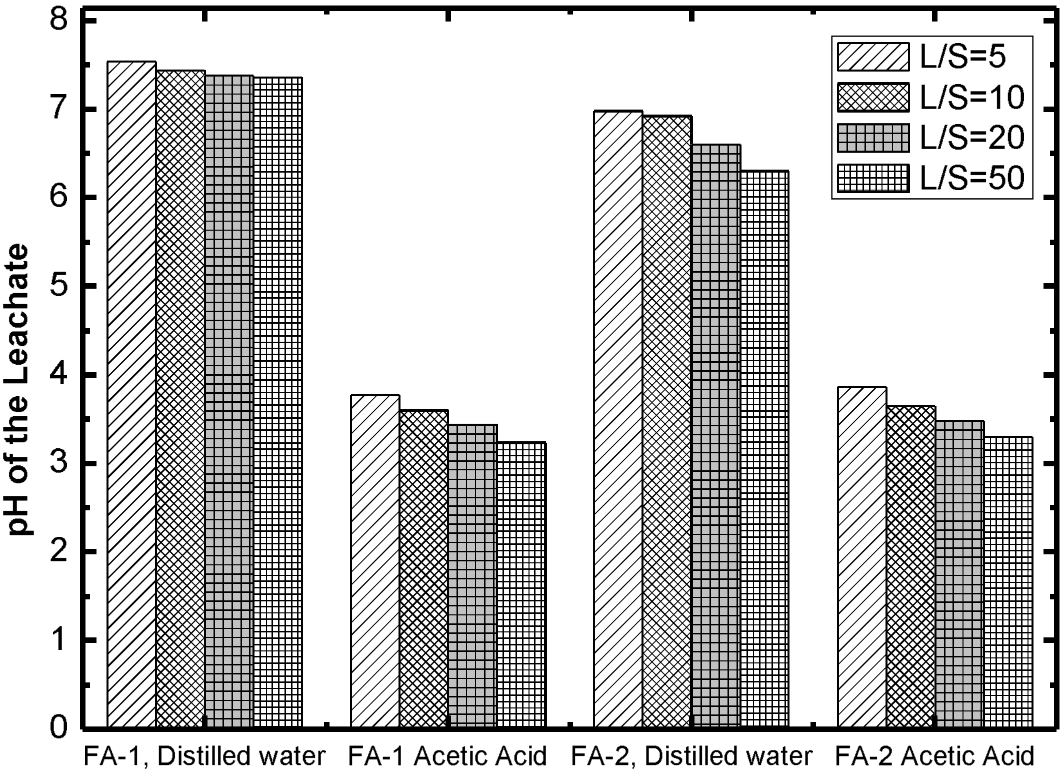


**Fig. 4.7** pH of leachate under different L/S ratio from leaching test results

**Table 4.1** Observed concentration of selected elements in representative leachate samples viz. FA-1 and FA-2 through TCLP and ASTM tests

| Elements | TCLP (mg/L) | | ASTM (mg/L) | | Drinking water limit as per WHO (mg/L) | Regulatory limits for TCLP prescribed by US EPA (mg/L)* |
|---|---|---|---|---|---|---|
| | FA 1 | FA 2 | FA 1 | FA 2 | | |
| **Al** | 50.13 | 23.1695 | 22.0445 | 0.346 | 0.1 | |
| **As** | 0.2845 | 0.0025 | 0.202 | 0.00375 | 0.01 | 5 |
| **Ba** | 1.1015 | 0.7175 | 0.485 | 0.1775 | 1.3 | 100 |
| **Ca** | 153.35 | 46.05 | 91.5 | 39.2 | - | - |
| **Cd** | 0.003 | 0.0005 | 0.001 | 0.0005 | 0.003 | 1 |
| **Co** | 0.036 | 0.0195 | 0.015 | 0.004 | - | |
| **Cr** | 0.2535 | 0.0725 | 0.1385 | 0.0095 | 0.05 | 5 |
| **Cu** | 0.159 | 0.2795 | 0.0695 | 0.007 | 2 | - |
| **Fe** | 2.45 | 17.59 | 1.2655 | 0.4985 | 0.1 | - |
| **Mg** | 50.5 | 26.9 | 33.45 | 17.45 | - | - |
| **Mn** | 0.943 | 1.234 | 0.403 | 0.164 | 0.05 | - |
| **Ni** | 0.089 | 0.0825 | 0.042 | 0.013 | 0.07 | - |
| **Pb** | 0.019 | 0.0285 | 0.013 | 0.0175 | 0.01 | 5 |
| **Se** | 0.1055 | 0.0055 | 0.0635 | 0.006 | 0.04 | 1 |
| **Si** | 49.65 | 33.85 | 25.1 | 7.15 | - | - |
| **Sr** | 0.9965 | 0.6605 | 0.575 | 0.515 | - | - |
| **Ti** | 0.282 | 0.1905 | 0.1785 | 0.048 | - | - |
| **V** | 0.87 | 0.0125 | 0.613 | 0.009 | - | - |
| **Zn** | 0.382 | 0.315 | 0.161 | 0.0815 | 4 | - |

*Source: SW-846, US EPA 2004

Combined batch leaching of FA and CT for, both acetic acid and distilled water are presented in Fig. 4.8 to Fig. 4.41 along with the comparison with individual FA and CT concentration and WHO prescribed standards. There are nine different mix combinations (detailed in Appendix A) of FA and CT samples, which are used to assess the immobilization behavior of FA combining with CT with regard to different heavy metals.

Batch leaching behaviour of combined and induvial FA and CT for Al is shown in Figs 4.8 and 4.9. In the TCLP test, Al concentration in the leachate is higher than the WHO standards in all the mix proportion. Its value is highest in Mix-9 sample. There is a progressive increase in the Al concentration from Mix-1 to Mix -9 samples. It shows that with the increase in FA concentration in the leaching medium, the Al concentration is trending to increase. Similar behaviour has been observed for ASTM leaching tests, but the values are nearly equivalent to WHO prescribed standards except for Mix-8 and Mix-9 samples.

Figs. 4.10 and 4.11 demonstrate the variation of As concentration in the leachate of TCLP and ASTM leaching tests, respectively. In TCLP tests, concentrations of As in all the mix combinations are found below WHO prescribed guidelines. However, in the case of ASTM tests, its concentration is higher in Mix 8 and Mix 9 samples than the WHO prescribed guidelines. Itreveals that the leaching of As in acidic leachant is lower than the distilled water, and an increase in FA content leads to a higher leaching of As.

Leaching behaviour of Ba has been shown in Fig. 4.12, and Fig. 4.13 for TCLP and ASTM tests, respectively. The concentration of Ba for all the mix proportions is below the WHO prescribed guidelines. But higher leaching has been observed in the acidic medium as compared to that in the case of distilled water. This confirms that Ba is more soluble in acidic medium. The concentration of Ba in different leachate increases with an increase in FA concentration for both TCLP and ASTM tests of leachates.

Figs. 4.14 and 4.15 show variation of Cd concentration of leachate using TCLP and ASTM tests, respectively. It is relatively below the WHO prescribed guidelines for all the Mix proportions. The leaching of Cd is higher in acidic medium, but no proper trends have been observed with variation in FA and CT concentrations.

Concentrations of Co in leachates using TCLP and ASTM tests are shown in Fig 4.16 and Fig. 4.17 respectively. Though there is no prescribed standard set by WHO for Co, it has been observed that the leaching of Co is higher in acidic leachant, and it decreases with a decrease in FA proportion.

Fig. 4.18, and Fig. 4.19 show Cr concentration in the leachates using TCLP and ASTM tests, respectively. The concentration of Cr is below the WHO prescribed limit in the leachate of all the Mix proportions; however, its value is higher in acidic medium. There is no variation observed in

TCLP tests of leachate for different mix proportions, but in the case of ASTM tests, the concentration increases with the increase in CT values.

Cu concentrations in leachates are detailed in Figs. 4.20 and 4.21 corresponding to TCLP and ASTM tests, respectively. The Cu values are below the WHO prescribed guidelines in the case of both tests of leachate. The leaching of Cu is significantly higher in all mix proportions for acidic leachant. In ASTM tests, the leaching values have been observed very less in all Mix proportions.

Fig. 4.22, and Fig. 4.23 show the concentration of Fe in leachate using TCLP and ASTM tests, respectively. The concentration of Fe is significantly higher than WHO prescribed guidelines in the case of TCLP tests of leachate for all the Mix proportions. However, in ASTM tests for leachate, values are fairly below the guidelines. It demonstrates higher leaching of Fe in acidic leachant. In TCLP tests, the concentration of Fe in leachate reduces with the reduction in FA proportion in the mix.

There is no WHO prescribed guidelines set for the Mg concentration in drinking water. Figs. 4.24 and 4.25 demonstrate the leaching behavior of Mg in the leachate of different mix proportions. The leaching of Mg is observed higher in acidic medium, but its concentration has been reducing with the reduction in FA content in the mix in both test cases.

Figs. 4.26 and 4.27 show the variation in the concentration of Mn in the leachates using both tests. In TCLP tests, its concentration is very much higher than the prescribed value given by WHO. However, in ASTM tests, it is slightly higher in Mix-1, Mix-2, Mix-3, Mix-4, and Mix-5 and nearly equal in Mix-6 as compare to that prescribed by WHO. Its concentration is also decreasing with the reduction of FA content in the mix.

Ni concentrations in leachate are detailed in Figs. 4.28 and 4.29. In leachate of ASTM tests, the concentrations are considerably less than the WHO prescribed limit. However, in TCLP tests, concentrations of Ni are significantly higher than those prescribed under WHO guidelines for all mix proportions except Mix-8 and Mix-9. In both the tests, the Ni concentration is reduced with the reduction in FA content in the mix proportions.

Pb concentrations in the leachate didn't show any notable trends for the different mix proportions. Figs. 4.30 and 4.31 show that the concentration of Pb is well below the WHO guidelines in both the test cases.

Fig. 4.32, and Fig. 4.33 show concentrations of Se in the Leachates of TCLP and ASTM tests. The concentrations are well below the WHO guidelines in the leachates of both the tests. The values are also nearly similar. These values have been observed to increase with the increase in the CT content in the mix proportions.

For Sr and Ti concentrations, there is no standard set by WHO. Fig. 4.34, Fig 4.35, Fig. 4.36, and Fig 4.37 demonstrate that there is no specific pattern followed in different mix proportions about Sr and Ti concentrations in leachates of TCLP and ASTM tests.

Fig. 4.38, and Fig. 4.39 show V concentrations in the leachates of different mix proportions. There is no standard set by the WHO for V concentration. In both the tests, its concentration increases with increase in CT content in the mix proportions.

The concentrations of Zn in the leachates of both TCLP and ASTM tests are shown in Figs. 4.40 and 4.41, respectively. In both the tests, its value is fairly below the WHO prescribed limit, and there are no specific trends observed with the variation in FA and CT contents for the concentrations in leachates.

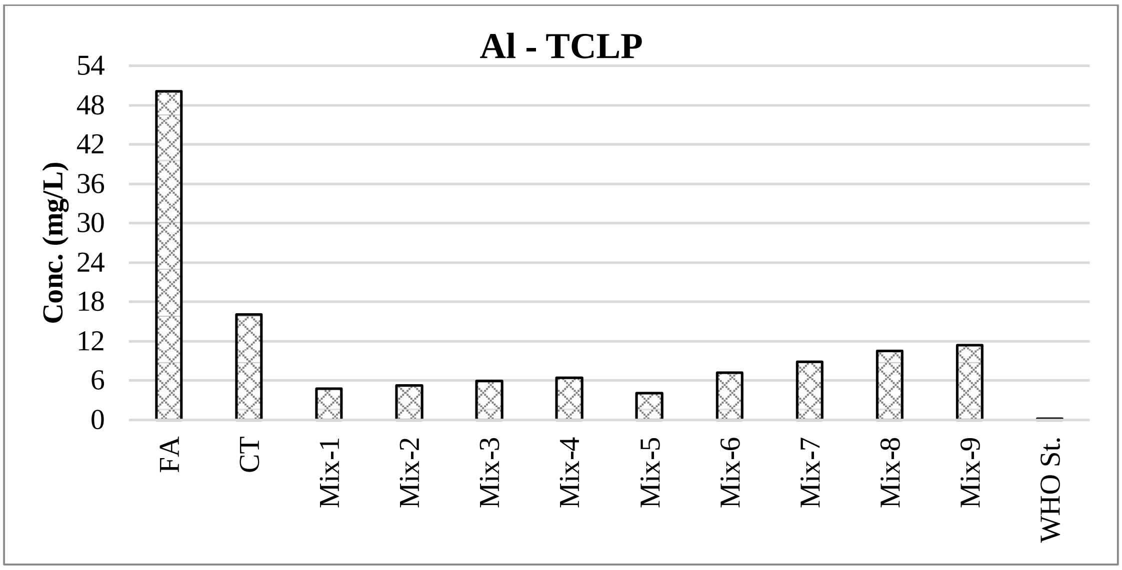


**Fig. 4.8** Concentration of Al in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

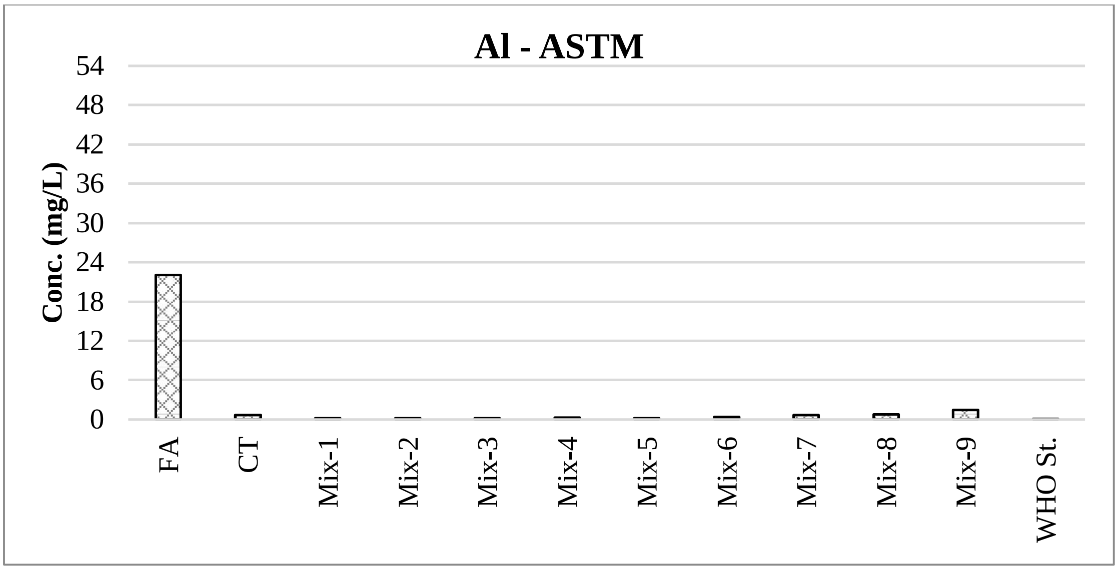


**Fig. 4.9** Concentration of Al in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

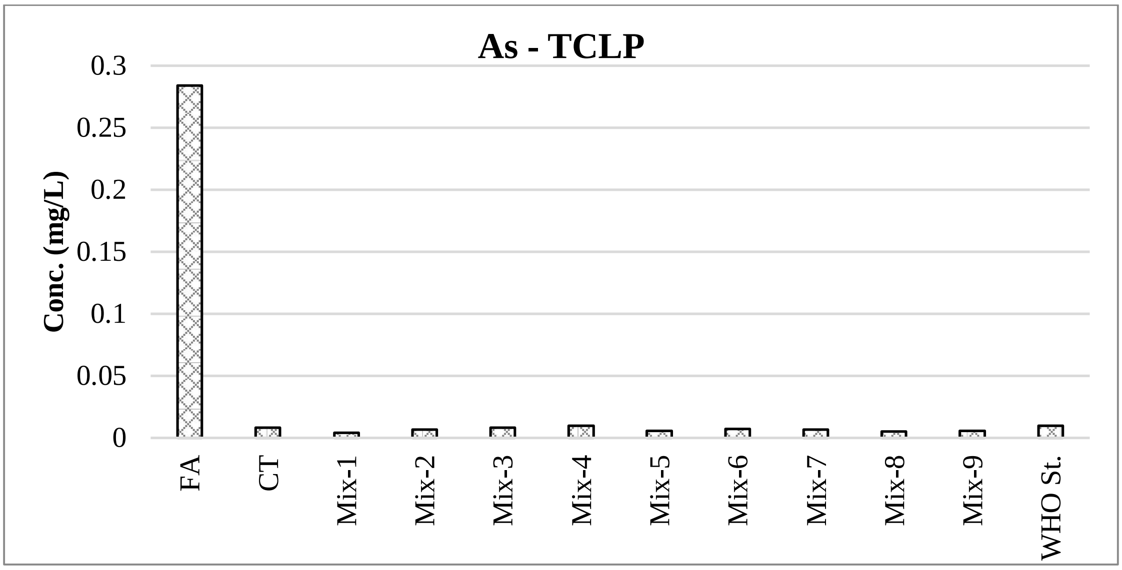


**Fig. 4.10** Concentration of As in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

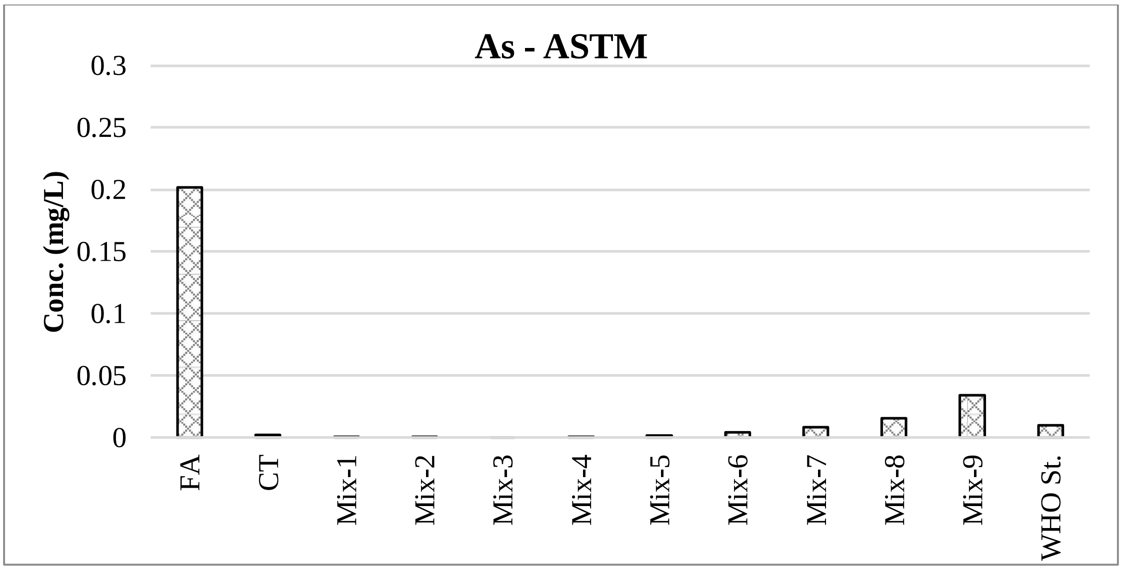


**Fig. 4.11** Concentration of As in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

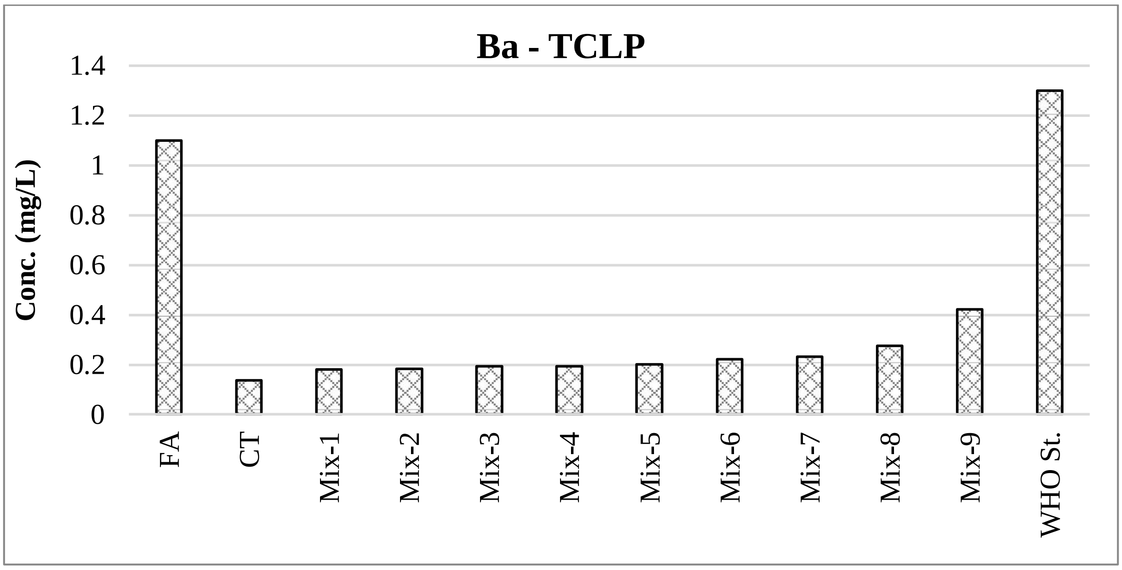


**Fig. 4.12** Concentration of Ba in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

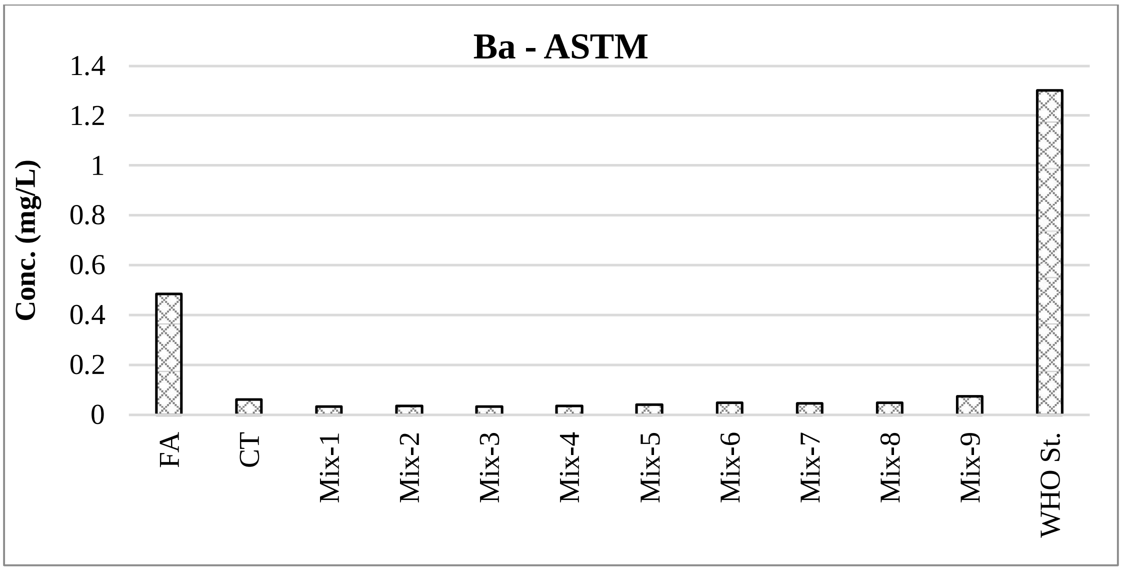


**Fig. 4.13** Concentration of BA in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

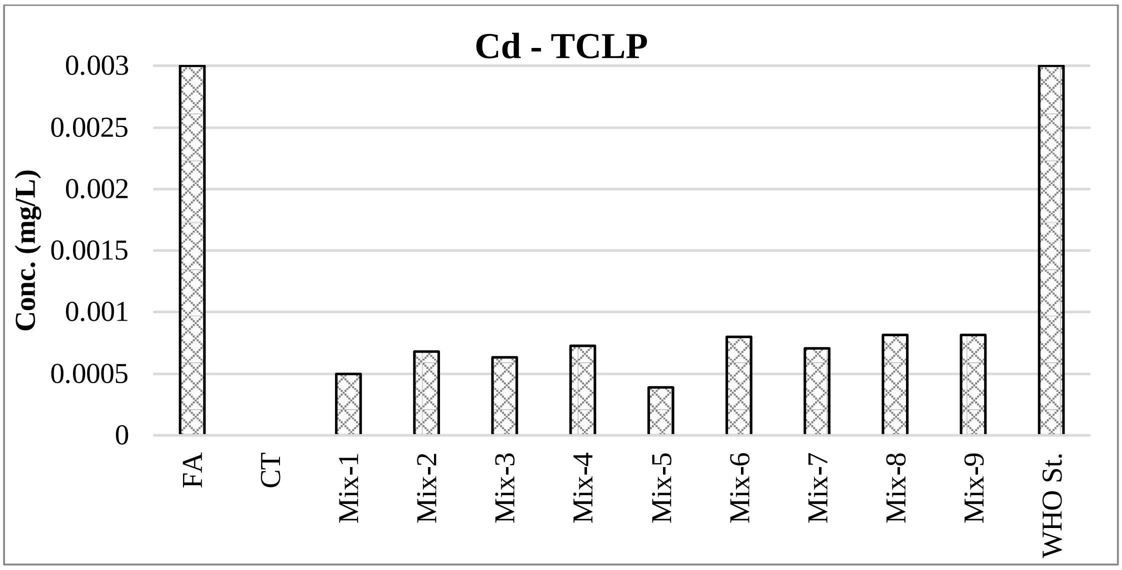


**Fig. 4.14** Concentration of Cd in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

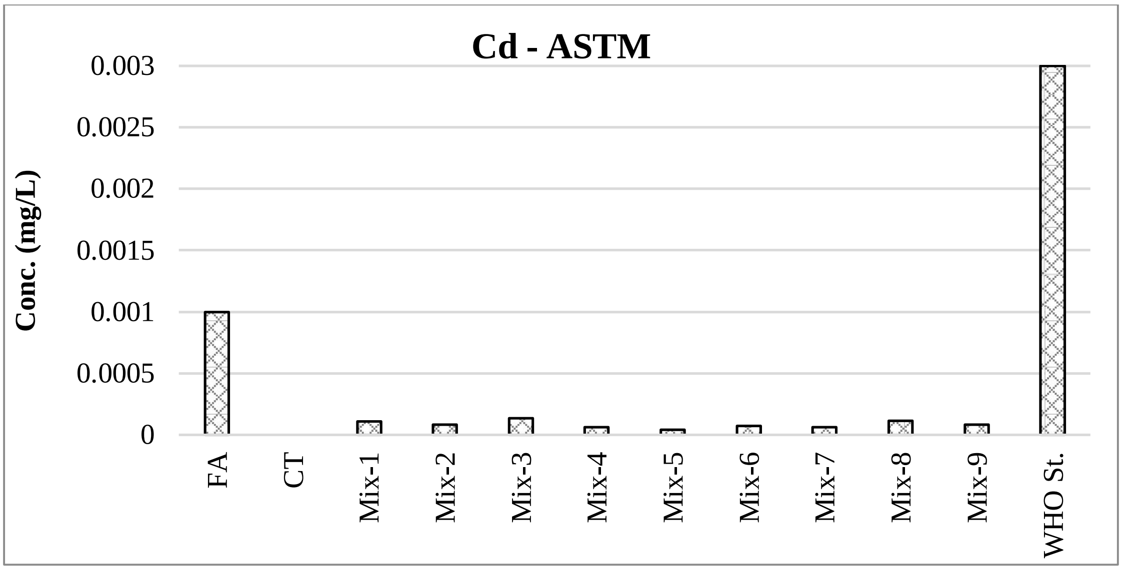


**Fig. 4.15** Concentration of Cd in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

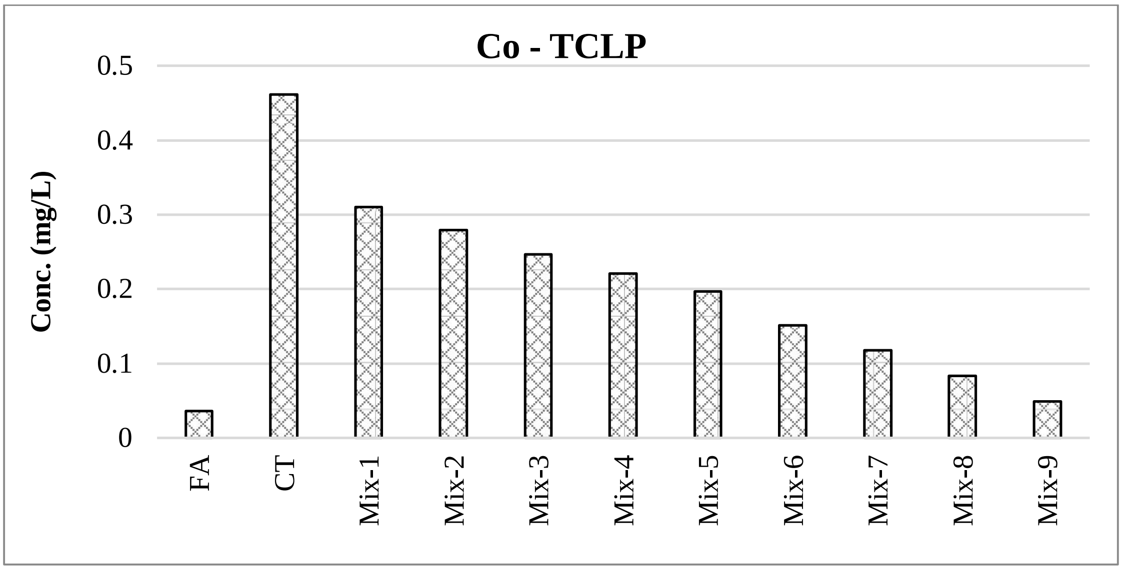


**Fig. 4.16** Concentration of Co in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

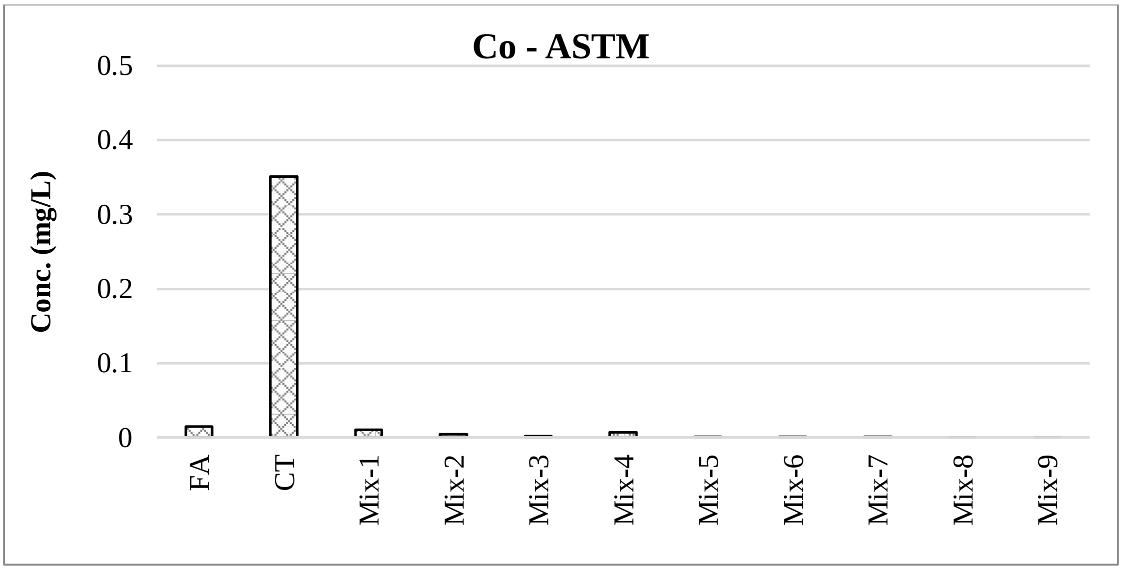


**Fig. 4.17** Concentration of Co in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

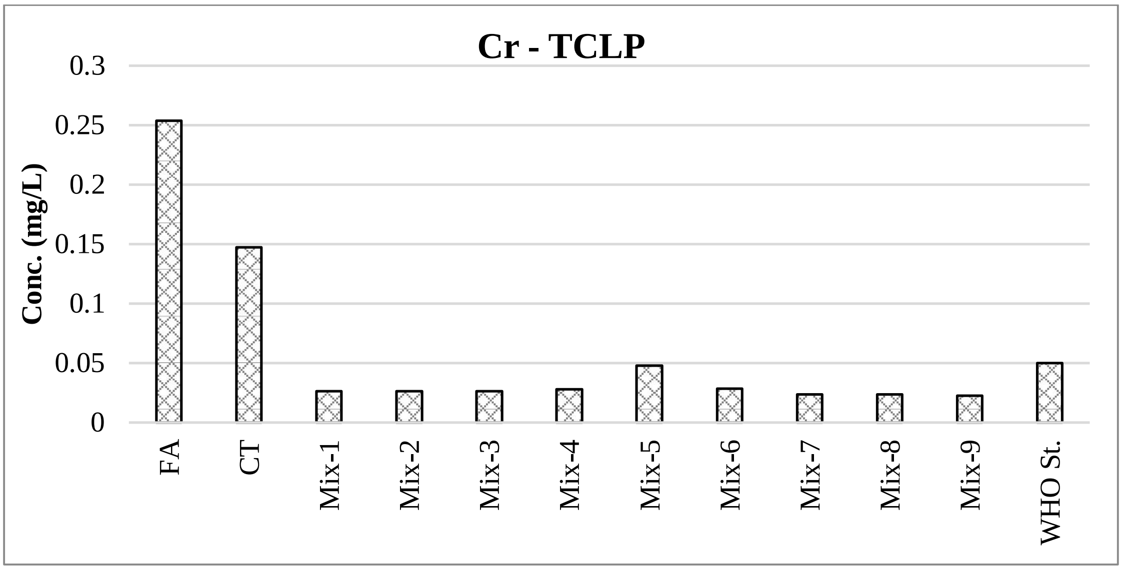


**Fig. 4.18** Concentration of Cr in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

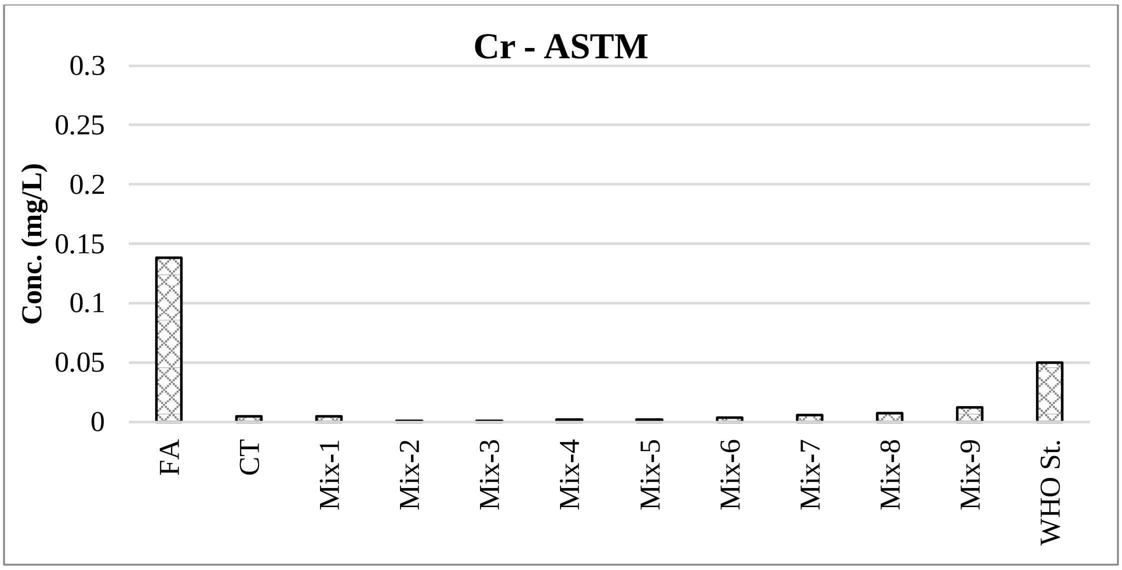


**Fig. 4.19** Concentration of Cr in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

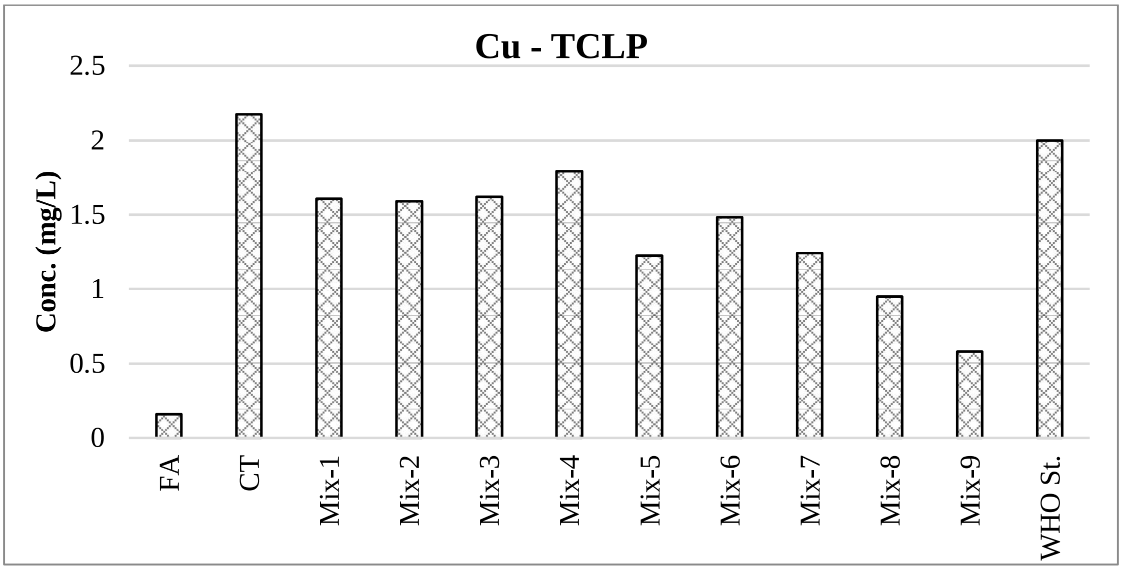


**Fig. 4.20** Concentration of Cu in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

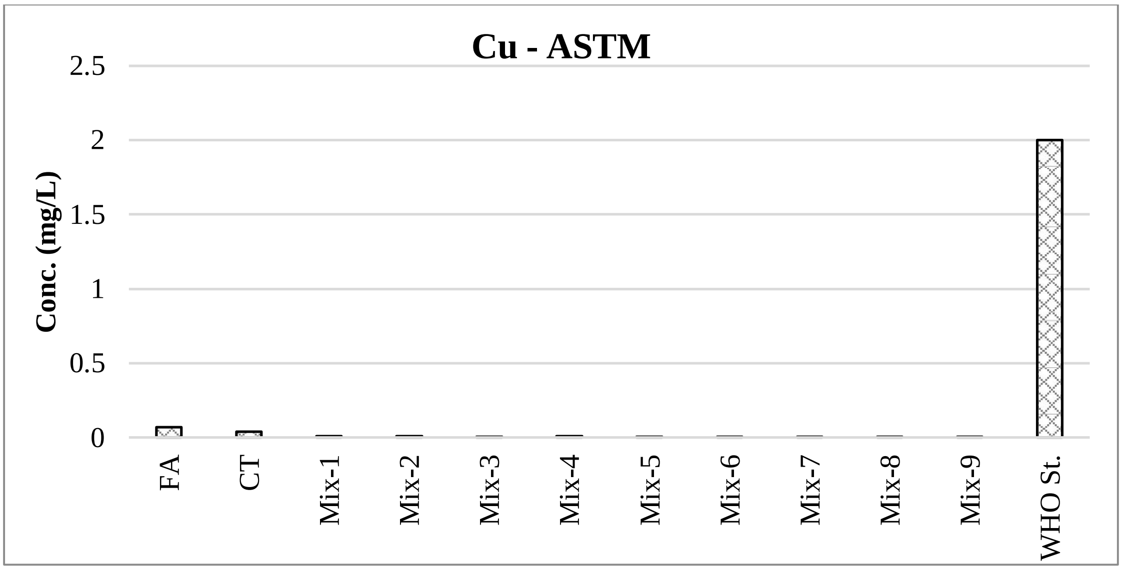


**Fig. 4.21** Concentration of Cu in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

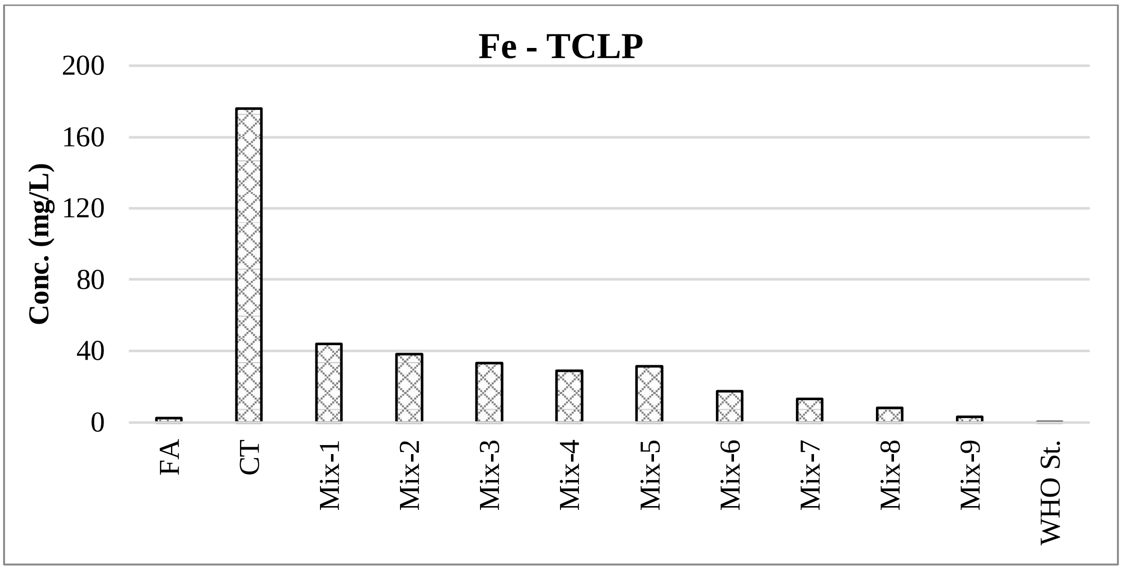


**Fig. 4.22** Concentration of Fe in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

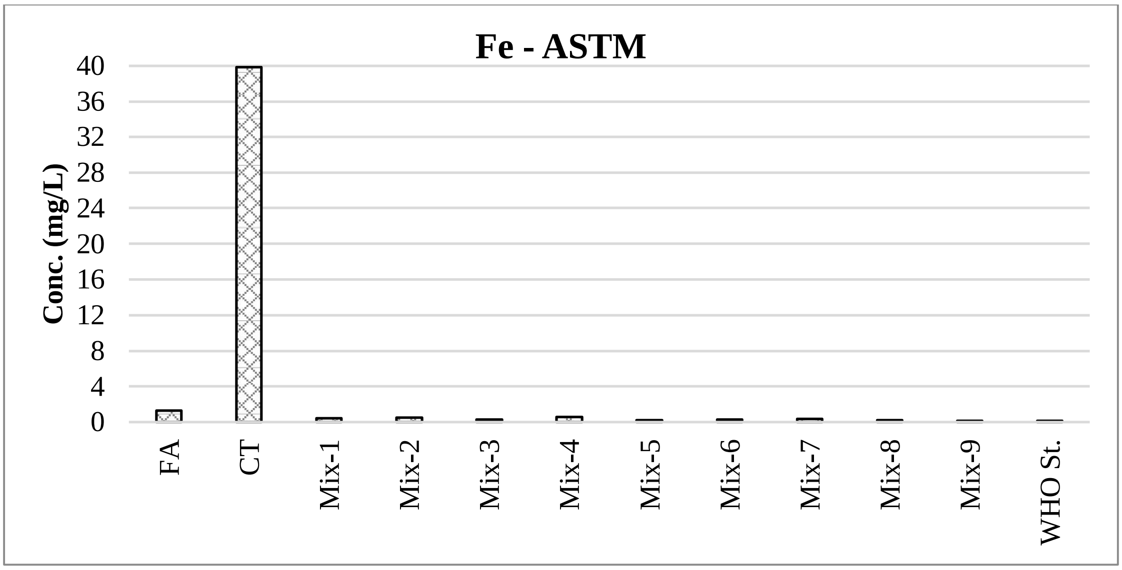


**Fig. 4.23** Concentration of Fe in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

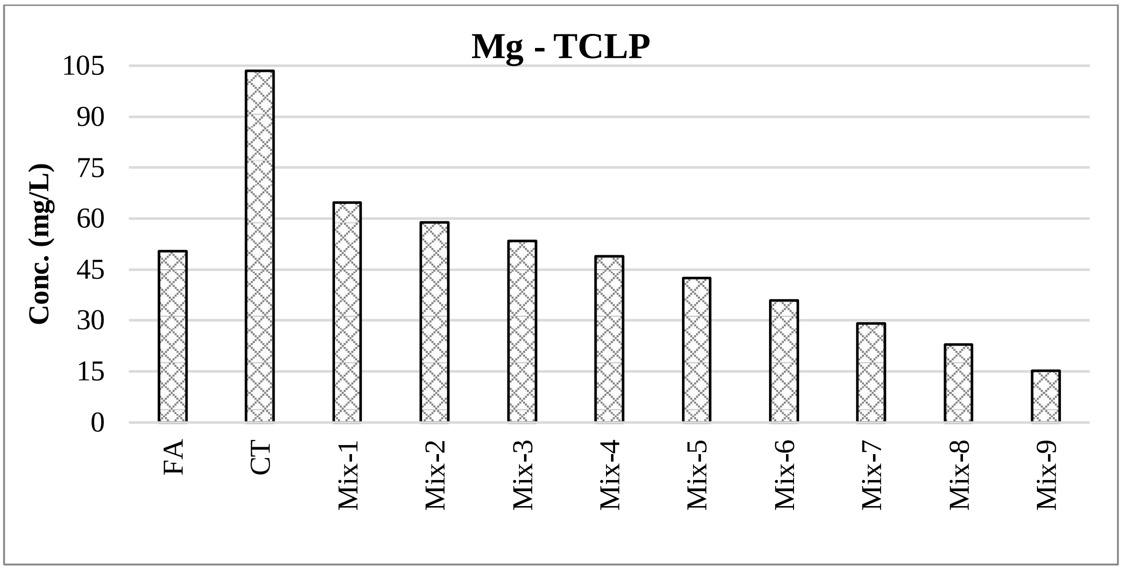


**Fig. 4.24** Concentration of Mg in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

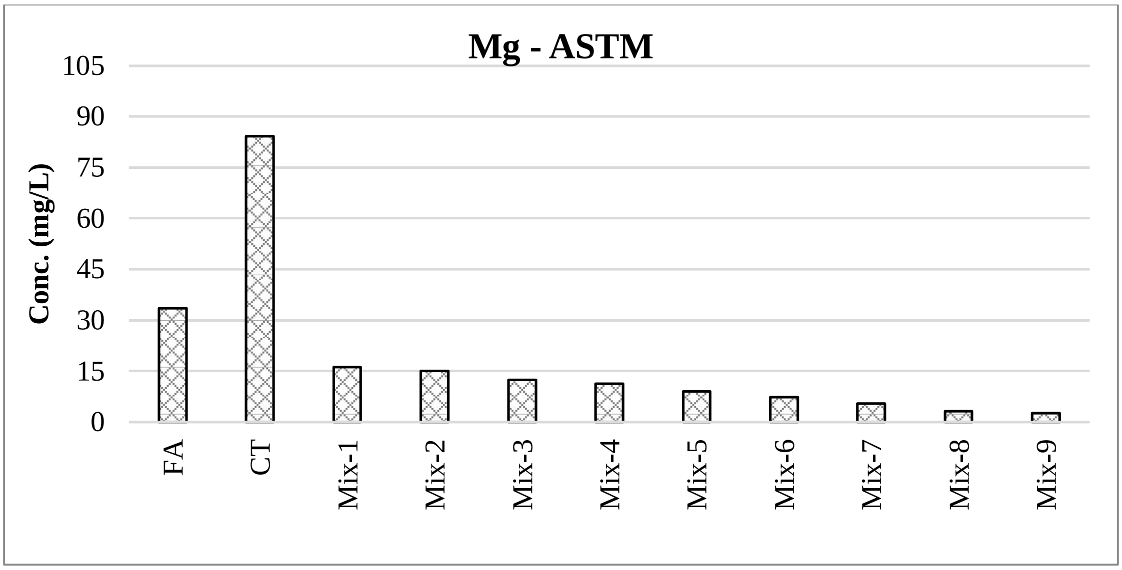


**Fig. 4.25** Concentration of Mg in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

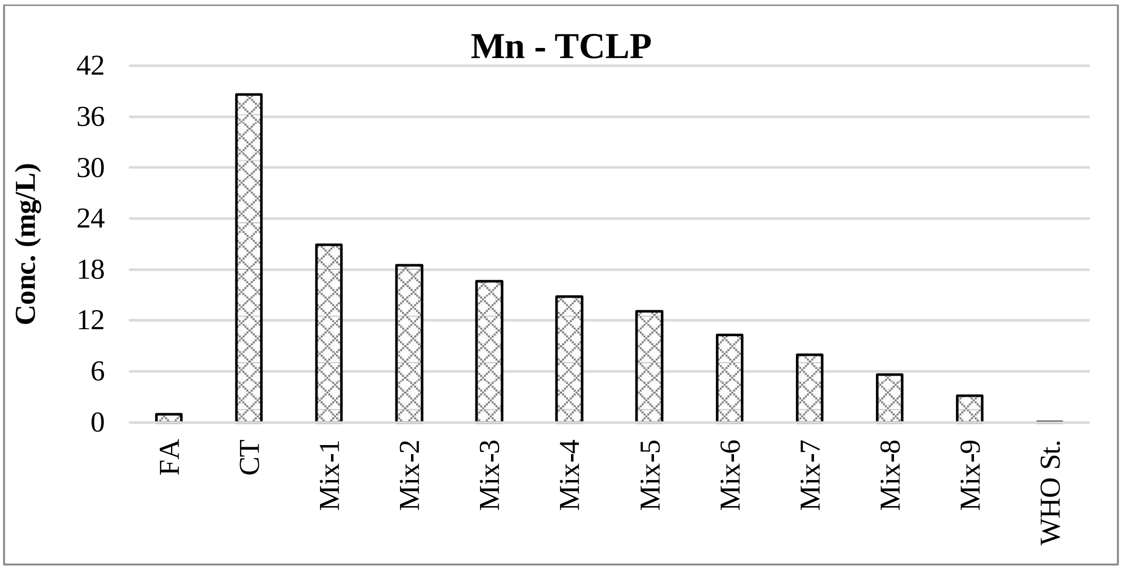


**Fig. 4.26** Concentration of Mn in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

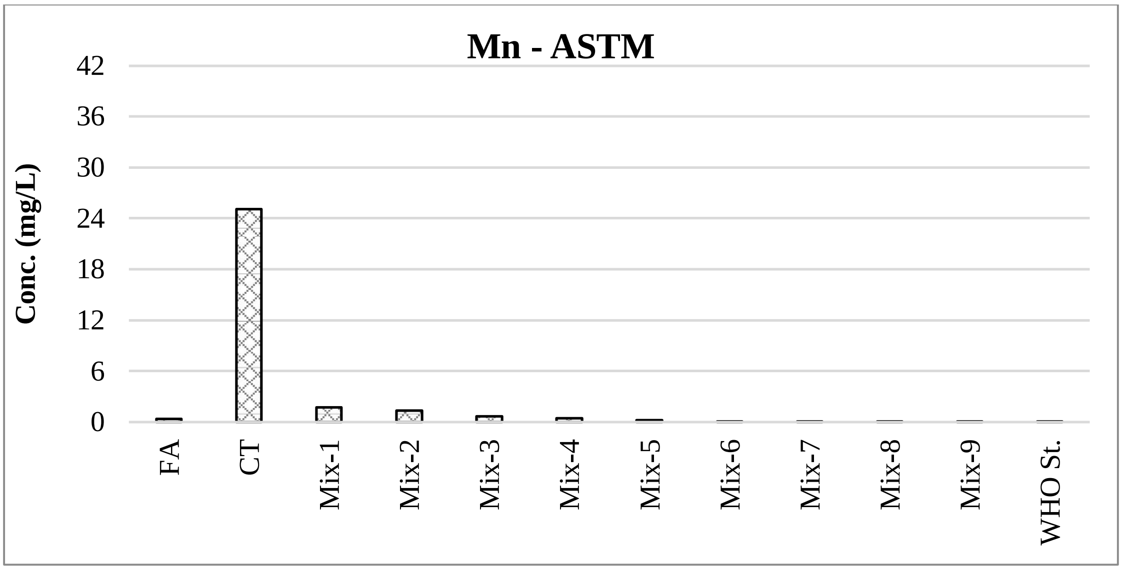


**Fig. 4.27** Concentration of Mn in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

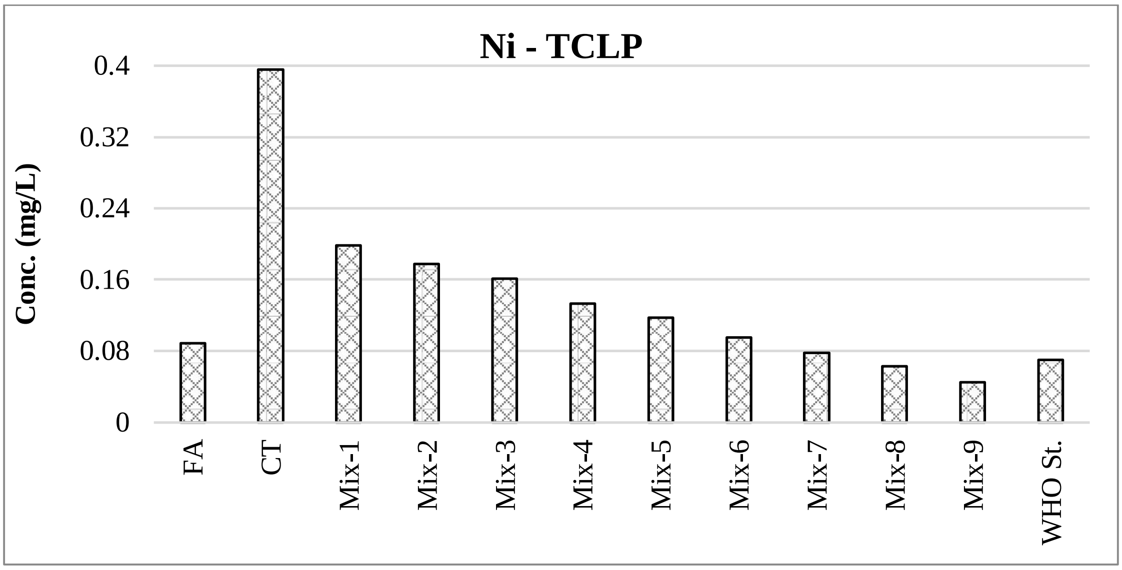


**Fig. 4.28** Concentration of Ni in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

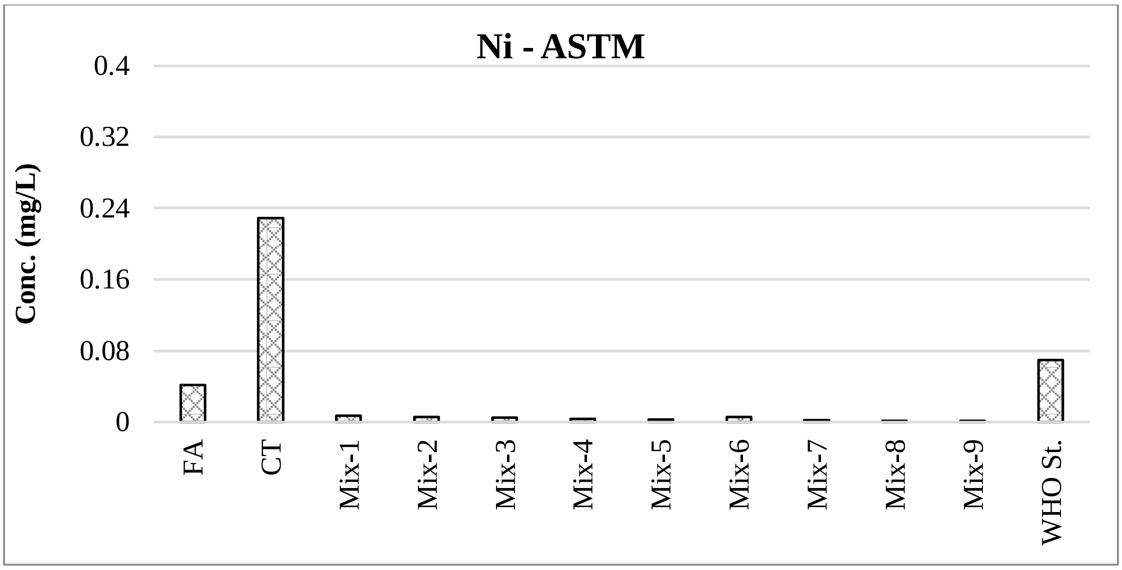


**Fig. 4.29** Concentration of Ni in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

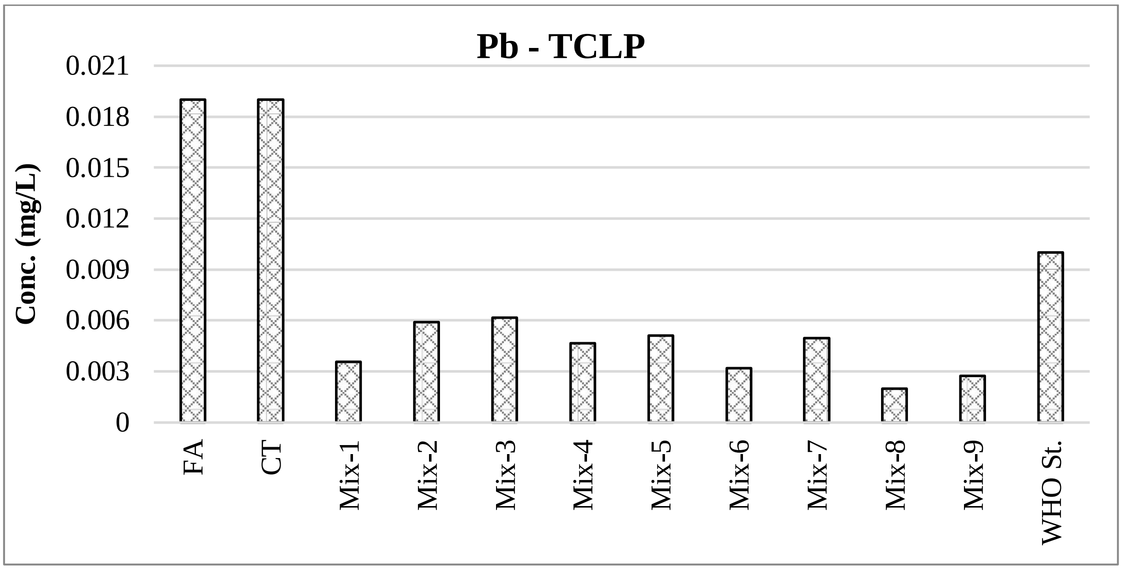


**Fig. 4.30** Concentration of Pb in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

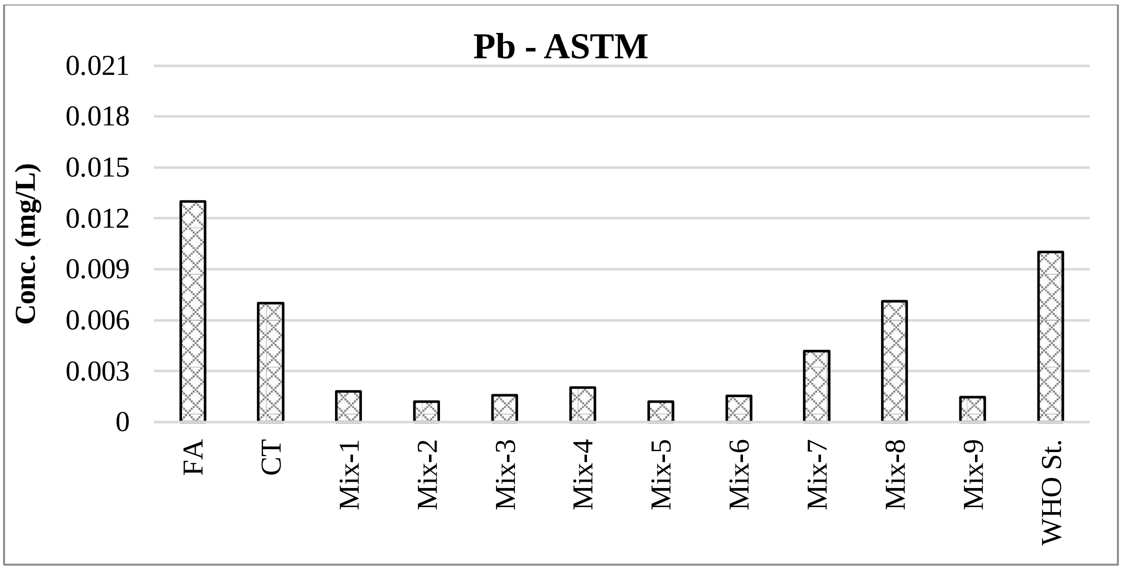


**Fig. 4.31** Concentration of Pb in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

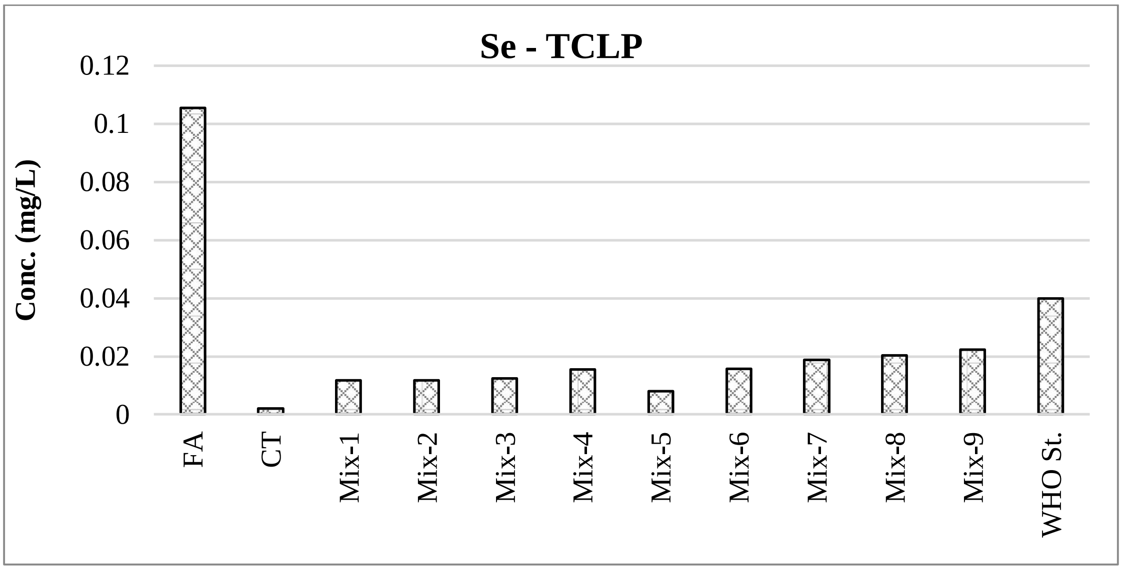


**Fig. 4.32** Concentration of Se in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

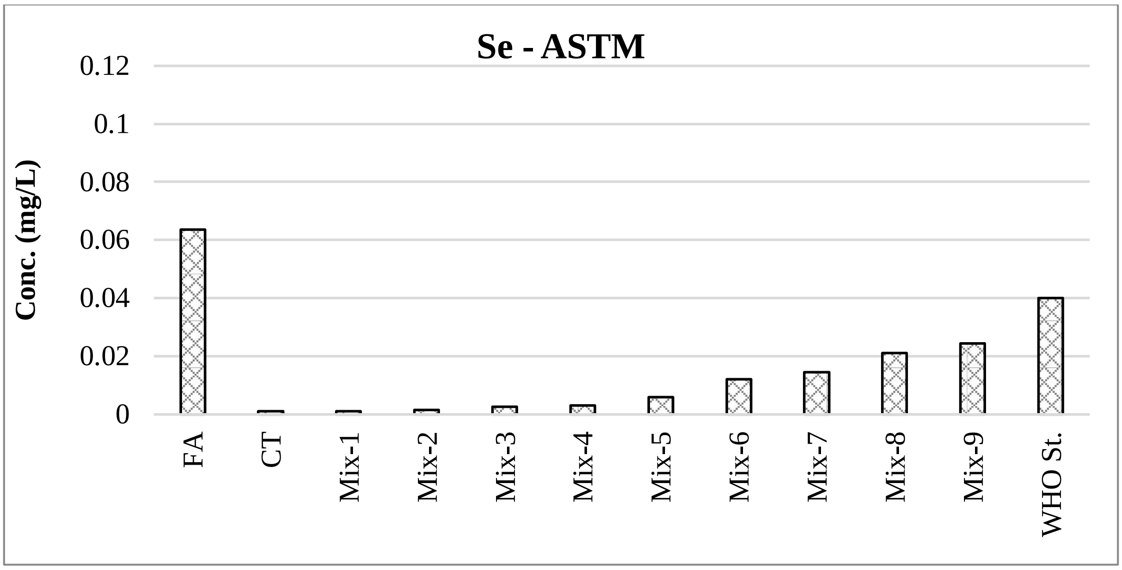


**Fig. 4.33** Concentration of Se in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

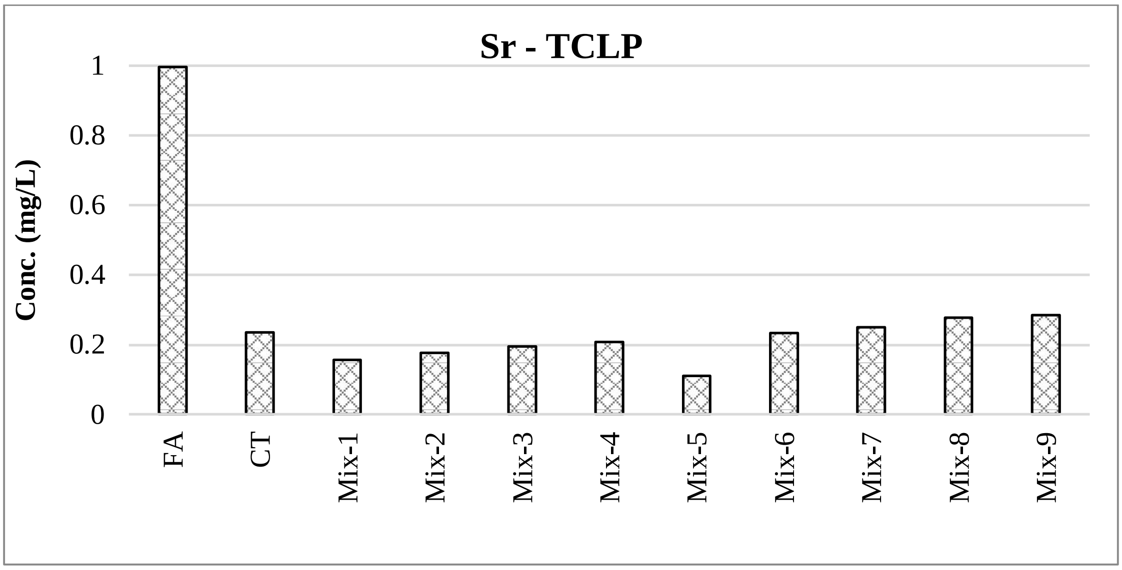


**Fig. 4.34** Concentration of Sr in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

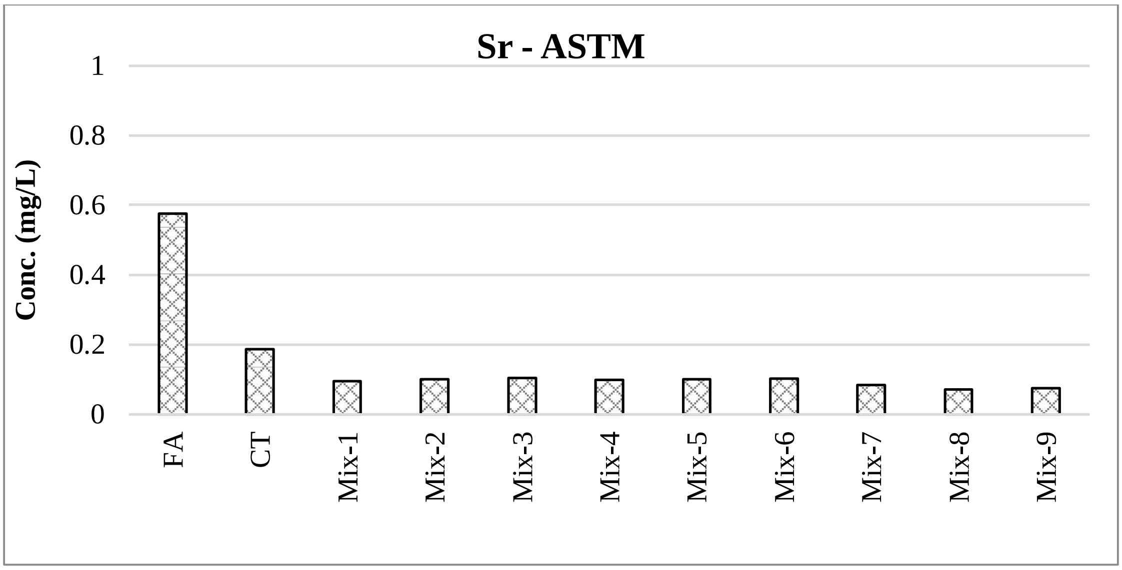


**Fig. 4.35** Concentration of Sr in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

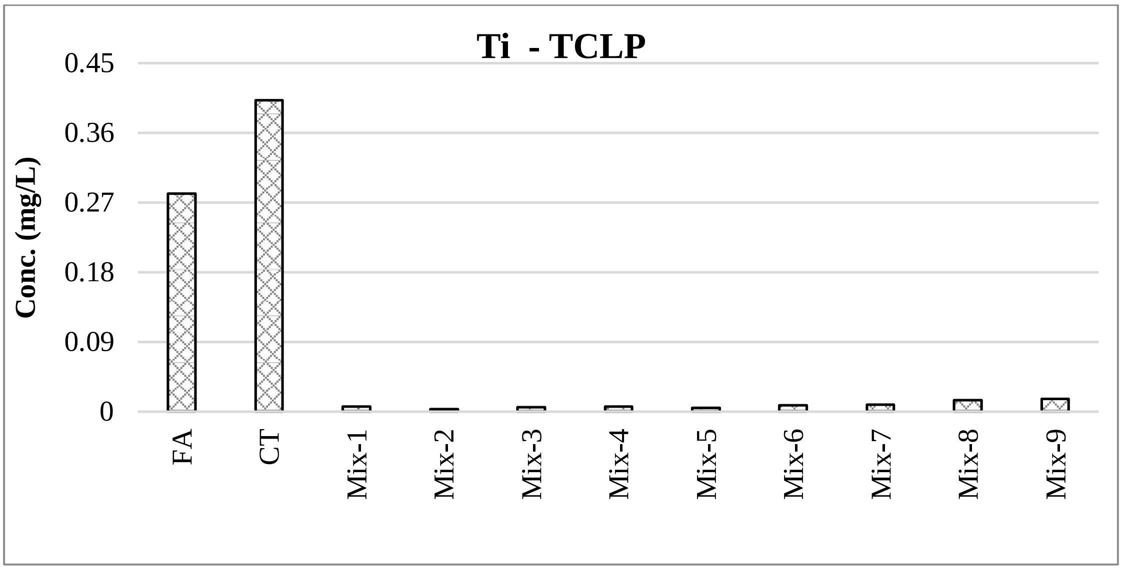


**Fig. 4.36** Concentration of Ti in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

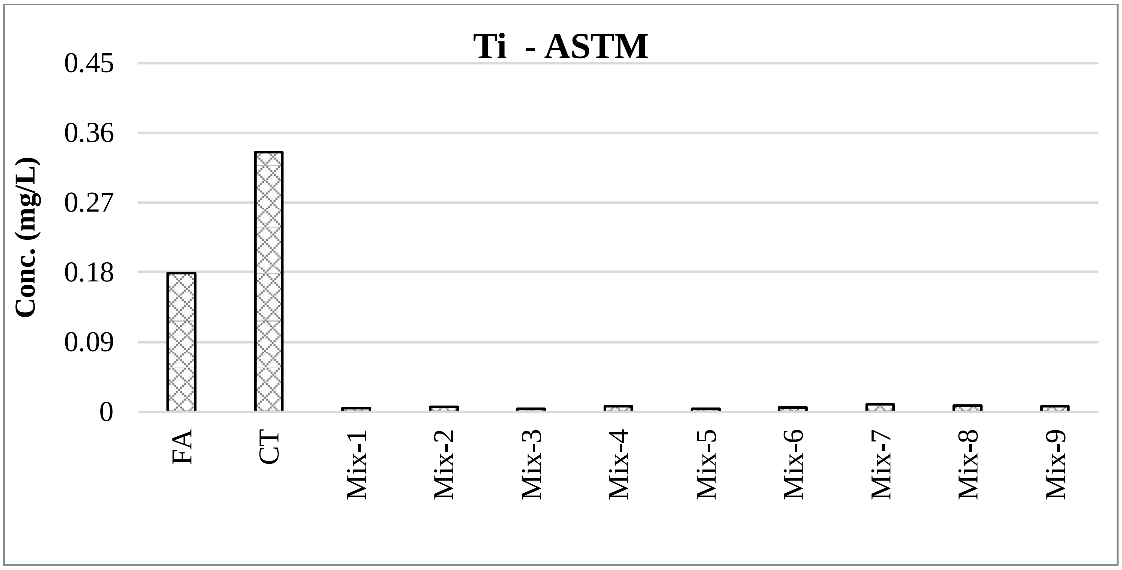


**Fig. 4.37** Concentration of Ti in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

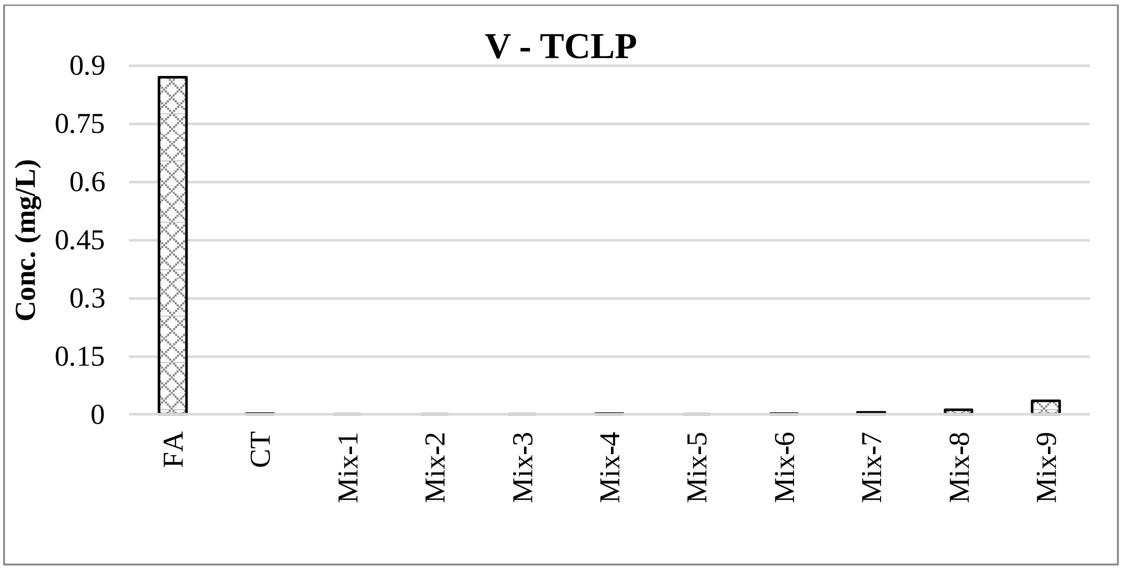


**Fig. 4.38** Concentration of V in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

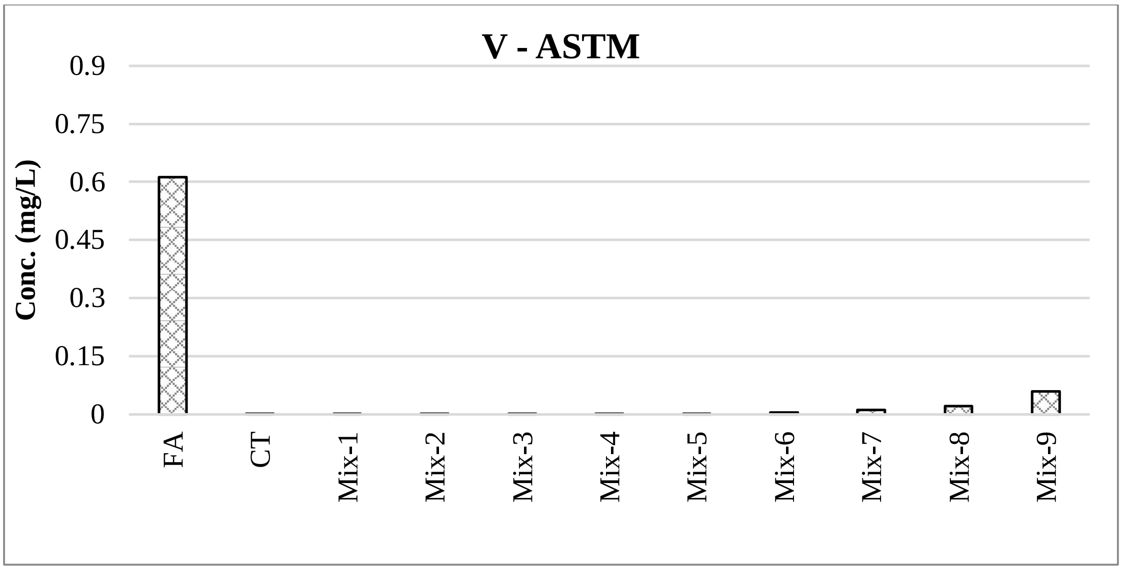


**Fig. 4.39** Concentration of V in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

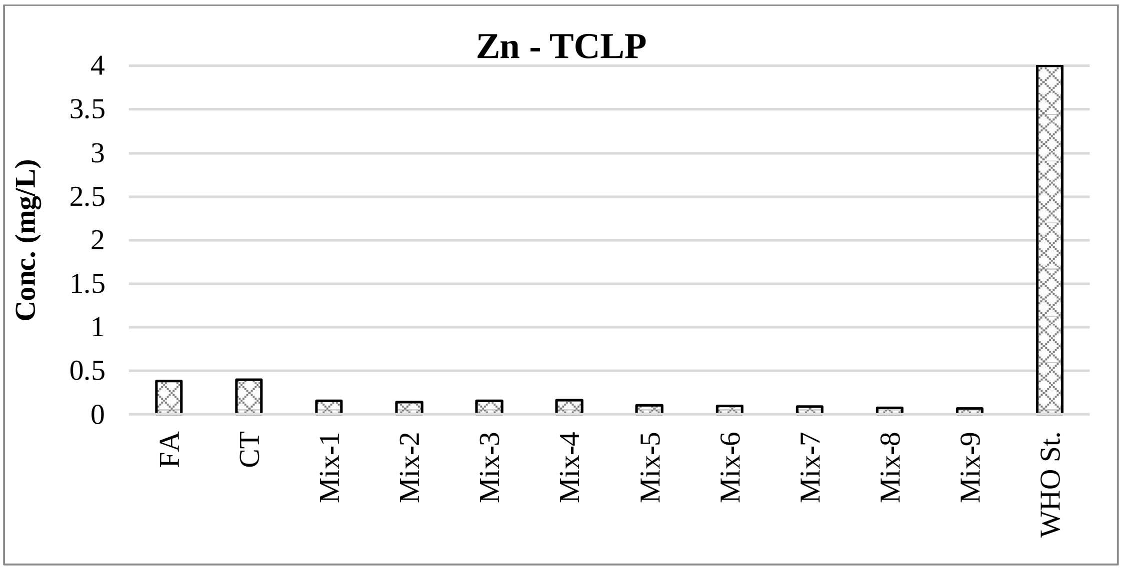


**Fig. 4.40** Concentration of Zn in leachate of TCLP batch leaching test for FA and CT individually and in combination of different mix proportions

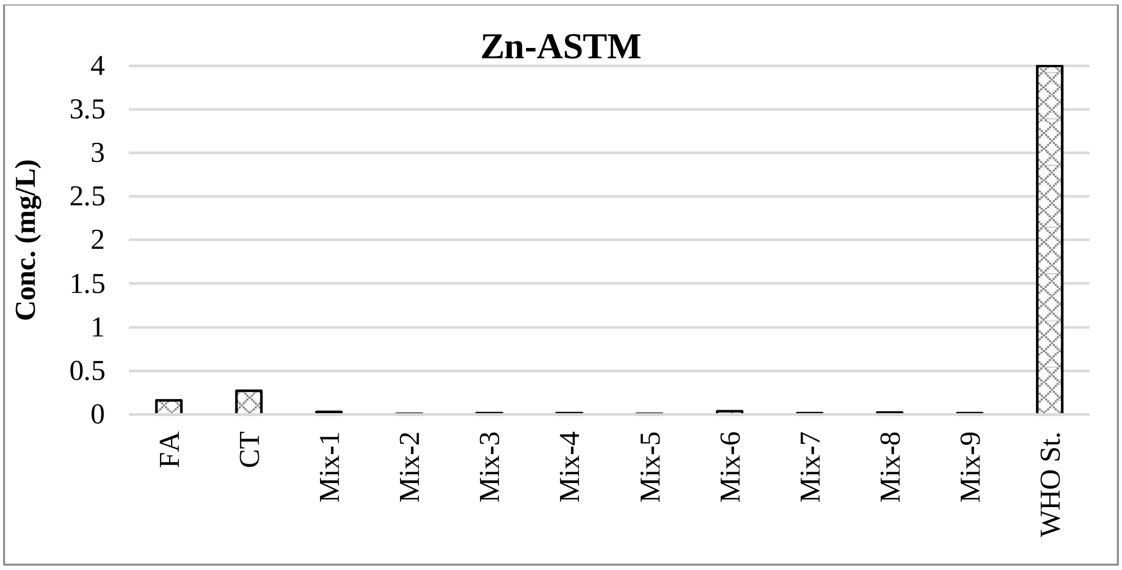


**Fig. 4.41** Concentration of Zn in leachate of ASTM batch leaching test for FA and CT individually and in combination of different mix proportions

The variation of elemental concentrations in leachate of different mix proportions is studied through the regression analysis. The results of the regression analysis are detailed in Table 4.2 and Table 4.3.

In combined TCLP batch leaching test, it can be said that the pH value of leachate is positively correlated with the concentration of Co, Cu, Fe, Mg, and Mn. The correlation of Al, Ba, Ti and V are negatively correlated with pH value. The FA and CT ratio is negatively correlated with pH and Cu but positively correlated with Ba and V. Concentrations of Al, Ba, Ti, and V is negatively correlated with the pH value, but Cu, Fe, Mg, and Mn are positively correlated with pH value. In the case of ASTM batch leaching test, the pH value does not show any correlation with the ratio of FA and CT. However, Al, As, Ba, Cr, Se, and V are positively correlated with FA/CT ratio.

### 4.4.3 Column leaching test results

The column leaching experiments were conducted for three different leachants; distilled water (DW), distilled water acidified to pH 2.88 by using acidic acid (acidic leachant) and alkalized to pH 11.2 by NaOH (alkaline leachant), to resemble different environmental conditions. The column test results are presented in Fig. 4.42 to Fig 4.58.

The temporal variation in the concentrations of Al in the leachate of column leaching tests for a different kind of leachates is detailed in Fig. 4.42. For all the tests the concentration is well below WHO standards except in the leachate of the initial 16 hrs of DW leachant. The concentration follows nearly similar for all the leachants. In all the cases, the Al concentration values are less than the concentration in leachant, which indicate possible sorption of Al in the material.

Fig. 4.43 shows the variation of As concentrations in the leachates of column tests. It is well below the WHO standards for all the leachants except for DW in the initial 16 hrs. The values have been observed to be higher than the concentration in leachant. Hence, there is a possibility of release of As from the column material and mixed to the leachant.

The temporal variation in Ba concentration in the leachates of column leaching tests are presented in Fig. 4.44. The values are significantly below WHO prescribed guidelines for all the three cases. Also, there are chances of sorption to the column material as the concentrations of Ba is higher in Leachant than leachate.

The variation of Cd concentration in the leachates of column experiments is detailed in Fig. 4.45. These are also well below the WHO prescribed limit. Initially, there is a possibility of release of Cd from column material to leachant in DW leachant. But as time passes the sorption phenomena is predominant, which may be the cause of the reduction in Cd concentration in leachate.

Fig 4.46 shows the Co concentrations in leachates of column experiments. Initially, there are some leaching of Co observed (mainly in acidic and DW leachant), but as the time passes, no variations in the concentrations of Co in leachate has been observed.

The Cr concentrations in the leachates of column test, presented in Fig. 4.47 is well below the WHO prescribed standards. For all the leachant, it shows nearly similar trends. Sorption of Cr may be possible in all the leachant as the concentrations of Cr in leachants are higher than the leachates.

Fig. 4.48 shows the Cu concentrations in the column test leachates. The values are considerably below the guidelines, which have identical leaching in all the leachants.

The Fe concentrations in the column leaching test are presented in Fig. 4.49. At the early stage of leaching in alkaline and DW leachants, its concentration is high, but at the later stage, it is reduced and becomes lower than the standards. However, in acidic leachant, it is very much higher (85.04 mg/L) than the standards in leachates collected after 64 hrs.

Concentrations of Mg in leachate of column test are detailed in Fig. 4.50. Leaching of Mg is predominant in all the leachants initially, but it is reduced with time in DW and alkaline leachants. In acidic leachant, leaching continues, which results in the concentration to become higher than that for other leachants.

Concentrations of Mn, presented in Fig. 4.51, is notably higher than the WHO permissible guidelines in leachates of all the test samples. In alkaline and DW leachates its value has been reduced as the time passes, but for acidic leachant, it remains higher than the prescribed standards.

Fig. 4.52 shows the concentration of Ni in the leachates of all the leachants. Initially, the value is higher than the standards for the leachants, but later it reduces, and only the concentration in the leachate of acidic leachant is above (0.16 mg/L after leachate of 130 hrs) the prescribed guidelines.

The Pb concentrations presented in Fig. 4.53 are considerably lower for all the leachants than the prescribed guidelines of WHO. In all the cases, sorption has been dominating after the initial interval of leachate collection as depicted in Fig. 4.53.

Fig. 4.54 details the results of column leaching tests for Se. All the collected leachate samples have concentration of Se below the WHO prescribed standards. Initially the concentrations of Se are high in all the samples, but at a later stage, it is identical with the concentration Se in leachants.

Sr concentrations in the samples of column tests are presented in Fig. 4.55. In all the cases concentration is high in earlier collected samples, but at a later stage it reduces. Acidic leachant shows higher leaching behaviour than than that for other leachants.

The concentrations of Ti in leachates of column tests are shown in Fig. 4.56. Earlier samples of leachates of acidic leachant shows highest Ti concentration, but at later stage the concentration in samples of DW leachate becomes higher than that for other leachants.

Fig. 4.57 shows the concentration of V in the column test. The DW leachants shows a higher concentration of V in the initial stage of leaching samples, but at a later stage, all three shows sorption of V to column material.

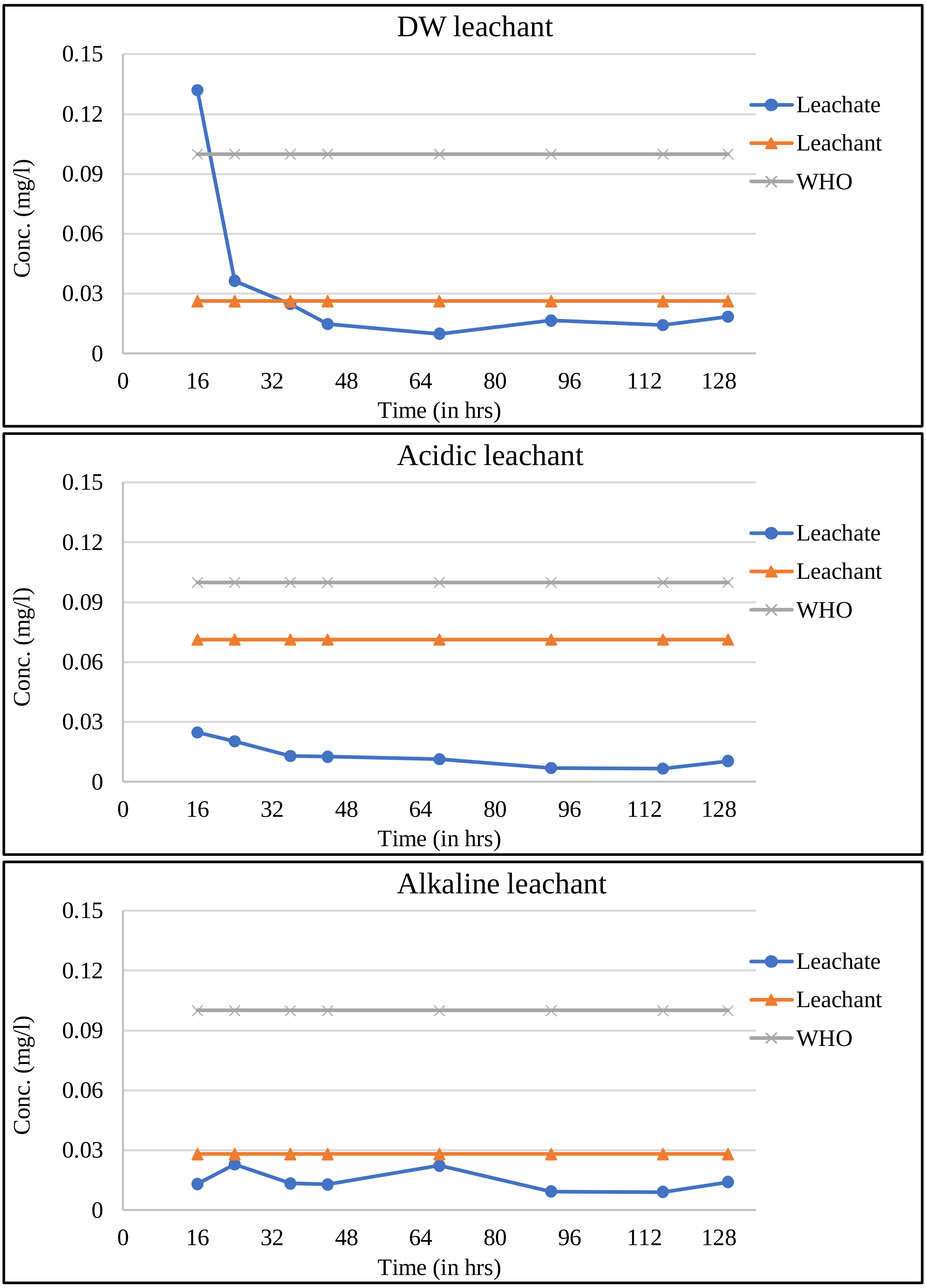
Zn concentrations, shown in Fig 4.58, in the leachates of all the lechants are considerably below the WHO guidelines. They follow nearly similar trends in all the collected leachate samples.

**Table 4.2** Regression analysis of combined (FA and CT) ASTM batch leaching tests results

| | FA/CT Ratio | pH | Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mg | Mn | Ni | Pb | Se | Sr | Ti | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FA/CT Ratio** | 1.00 | **-0.96** | 0.86 | -0.31 | **1.00** | 0.54 | -0.84 | -0.33 | **-0.92** | -0.83 | -0.85 | -0.85 | -0.80 | -0.61 | 0.79 | 0.72 | 0.89 | **0.99** | -0.76 |
| **pH** | **-0.96** | 1.00 | **-0.92** | 0.32 | **-0.95** | -0.60 | **0.93** | 0.36 | **0.94** | **0.92** | **0.93** | **0.93** | 0.89 | 0.60 | -0.83 | -0.79 | **-0.91** | **-0.91** | 0.87 |
| **Al** | 0.86 | -0.92 | 1.00 | | | | | | | | | | | | | | | | |
| **As** | -0.31 | 0.32 | -0.14 | 1.00 | | | | | | | | | | | | | | | |
| **Ba** | 1.00 | -0.95 | 0.85 | -0.29 | 1.00 | | | | | | | | | | | | | | |
| **Cd** | 0.54 | -0.60 | 0.80 | 0.26 | 0.54 | 1.00 | | | | | | | | | | | | | |
| **Co** | -0.84 | 0.93 | -0.89 | 0.14 | -0.82 | -0.62 | 1.00 | | | | | | | | | | | | |
| **Cr** | -0.33 | 0.36 | -0.61 | -0.03 | -0.33 | -0.74 | 0.22 | 1.00 | | | | | | | | | | | |
| **Cu** | -0.92 | 0.94 | -0.77 | 0.55 | -0.90 | -0.32 | 0.85 | 0.11 | 1.00 | | | | | | | | | | |
| **Fe** | -0.83 | 0.92 | -0.94 | 0.08 | -0.82 | -0.72 | 0.99 | 0.35 | 0.80 | 1.00 | | | | | | | | | |
| **Mg** | -0.85 | 0.93 | -0.89 | 0.16 | -0.83 | -0.60 | 1.00 | 0.20 | 0.86 | 0.98 | 1.00 | | | | | | | | |
| **Mn** | -0.85 | 0.93 | -0.89 | 0.14 | -0.83 | -0.61 | 1.00 | 0.21 | 0.85 | 0.99 | 1.00 | 1.00 | | | | | | | |
| **Ni** | -0.80 | 0.89 | -0.85 | 0.09 | -0.78 | -0.59 | 0.99 | 0.14 | 0.81 | 0.98 | 0.99 | 0.99 | 1.00 | | | | | | |
| **Pb** | -0.61 | 0.60 | -0.66 | 0.44 | -0.60 | -0.48 | 0.61 | 0.30 | 0.59 | 0.62 | 0.61 | 0.61 | 0.59 | 1.00 | | | | | |
| **Se** | 0.79 | -0.83 | 0.98 | -0.04 | 0.77 | 0.86 | -0.82 | -0.71 | -0.64 | -0.89 | -0.81 | -0.82 | -0.78 | -0.65 | 1.00 | | | | |
| **Sr** | 0.72 | -0.79 | 0.96 | 0.03 | 0.71 | 0.92 | -0.79 | -0.75 | -0.56 | -0.87 | -0.77 | -0.78 | -0.75 | -0.60 | 0.98 | 1.00 | | | |
| **Ti** | 0.89 | -0.91 | 0.94 | -0.31 | 0.88 | 0.65 | -0.86 | -0.49 | -0.83 | -0.87 | -0.86 | -0.86 | -0.81 | -0.80 | 0.89 | 0.85 | 1.00 | | |
| **V** | 0.99 | -0.91 | 0.82 | -0.31 | 0.99 | 0.51 | -0.76 | -0.37 | -0.88 | -0.76 | -0.77 | -0.76 | -0.71 | -0.58 | 0.75 | 0.68 | 0.86 | 1.00 | |
| **Zn** | -0.76 | 0.87 | -0.74 | 0.46 | -0.74 | -0.40 | 0.91 | 0.05 | 0.90 | 0.87 | 0.92 | 0.91 | 0.90 | 0.61 | -0.63 | -0.59 | -0.74 | -0.67 | 1.00 |

**Table. 4.3** Regression analysis of combined (FA and CT) TCLP batch leaching tests results

| | FA/CT Ratio | pH | Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mg | Mn | Ni | Pb | Se | Sr | Ti | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FA/CT Ratio** | 1.00 | -0.22 | **0.99** | **1.00** | **0.97** | -0.01 | -0.51 | **0.93** | -0.50 | -0.63 | -0.80 | -0.56 | -0.66 | 0.23 | **0.90** | -0.80 | 0.39 | **0.99** | -0.08 |
| **pH** | -0.22 | 1.00 | -0.20 | -0.16 | -0.23 | 0.62 | 0.57 | -0.06 | 0.48 | 0.40 | 0.55 | 0.76 | 0.72 | -0.11 | -0.31 | 0.12 | -0.11 | -0.13 | 0.36 |
| **Al** | 0.99 | -0.20 | 1.00 | | | | | | | | | | | | | | | | |
| **As** | 1.00 | -0.16 | 0.99 | 1.00 | | | | | | | | | | | | | | | |
| **Ba** | 0.97 | -0.23 | 0.97 | 0.96 | 1.00 | | | | | | | | | | | | | | |
| **Cd** | -0.01 | 0.62 | -0.06 | 0.03 | -0.12 | 1.00 | | | | | | | | | | | | | |
| **Co** | -0.51 | 0.57 | -0.50 | -0.47 | -0.58 | 0.19 | 1.00 | | | | | | | | | | | | |
| **Cr** | 0.93 | -0.06 | 0.94 | 0.94 | 0.91 | 0.07 | -0.33 | 1.00 | | | | | | | | | | | |
| **Cu** | -0.50 | 0.48 | -0.42 | -0.48 | -0.47 | -0.15 | 0.68 | -0.43 | 1.00 | | | | | | | | | | |
| **Fe** | -0.63 | 0.40 | -0.55 | -0.61 | -0.65 | -0.12 | 0.76 | -0.55 | 0.95 | 1.00 | | | | | | | | | |
| **Mg** | -0.80 | 0.55 | -0.82 | -0.78 | -0.83 | 0.19 | 0.79 | -0.76 | 0.62 | 0.71 | 1.00 | | | | | | | | |
| **Mn** | -0.56 | 0.76 | -0.57 | -0.51 | -0.63 | 0.36 | 0.86 | -0.45 | 0.56 | 0.64 | 0.91 | 1.00 | | | | | | | |
| **Ni** | -0.66 | 0.72 | -0.69 | -0.64 | -0.61 | 0.32 | 0.65 | -0.56 | 0.53 | 0.48 | 0.84 | 0.79 | 1.00 | | | | | | |
| **Pb** | 0.23 | -0.11 | 0.29 | 0.26 | 0.16 | 0.24 | -0.28 | 0.37 | -0.27 | -0.19 | -0.54 | -0.38 | -0.54 | 1.00 | | | | | |
| **Se** | 0.90 | -0.31 | 0.91 | 0.89 | 0.91 | -0.03 | -0.68 | 0.89 | -0.57 | -0.70 | -0.96 | -0.75 | -0.74 | 0.54 | 1.00 | | | | |
| **Sr** | -0.80 | 0.12 | -0.84 | -0.83 | -0.72 | -0.12 | 0.37 | -0.88 | 0.43 | 0.44 | 0.76 | 0.45 | 0.74 | -0.71 | -0.87 | 1.00 | | | |
| **Ti** | 0.39 | -0.11 | 0.52 | 0.41 | 0.37 | -0.20 | -0.20 | 0.47 | 0.18 | 0.16 | -0.52 | -0.38 | -0.62 | 0.67 | 0.54 | -0.70 | 1.00 | | |
| **V** | 0.99 | -0.13 | 0.98 | 0.99 | 0.95 | 0.05 | -0.41 | 0.93 | -0.46 | -0.59 | -0.72 | -0.46 | -0.59 | 0.17 | 0.85 | -0.79 | 0.36 | 1.00 | |
| **Zn** | -0.08 | 0.36 | -0.10 | -0.08 | 0.02 | 0.26 | 0.19 | 0.09 | 0.13 | -0.05 | 0.02 | 0.04 | 0.50 | -0.02 | 0.05 | 0.16 | -0.25 | -0.08 | 1.00 |



DW leachant

Acidic leachant

Alkaline leachant

**Fig. 4.42** Al concentration in column leaching results for different types of leachant

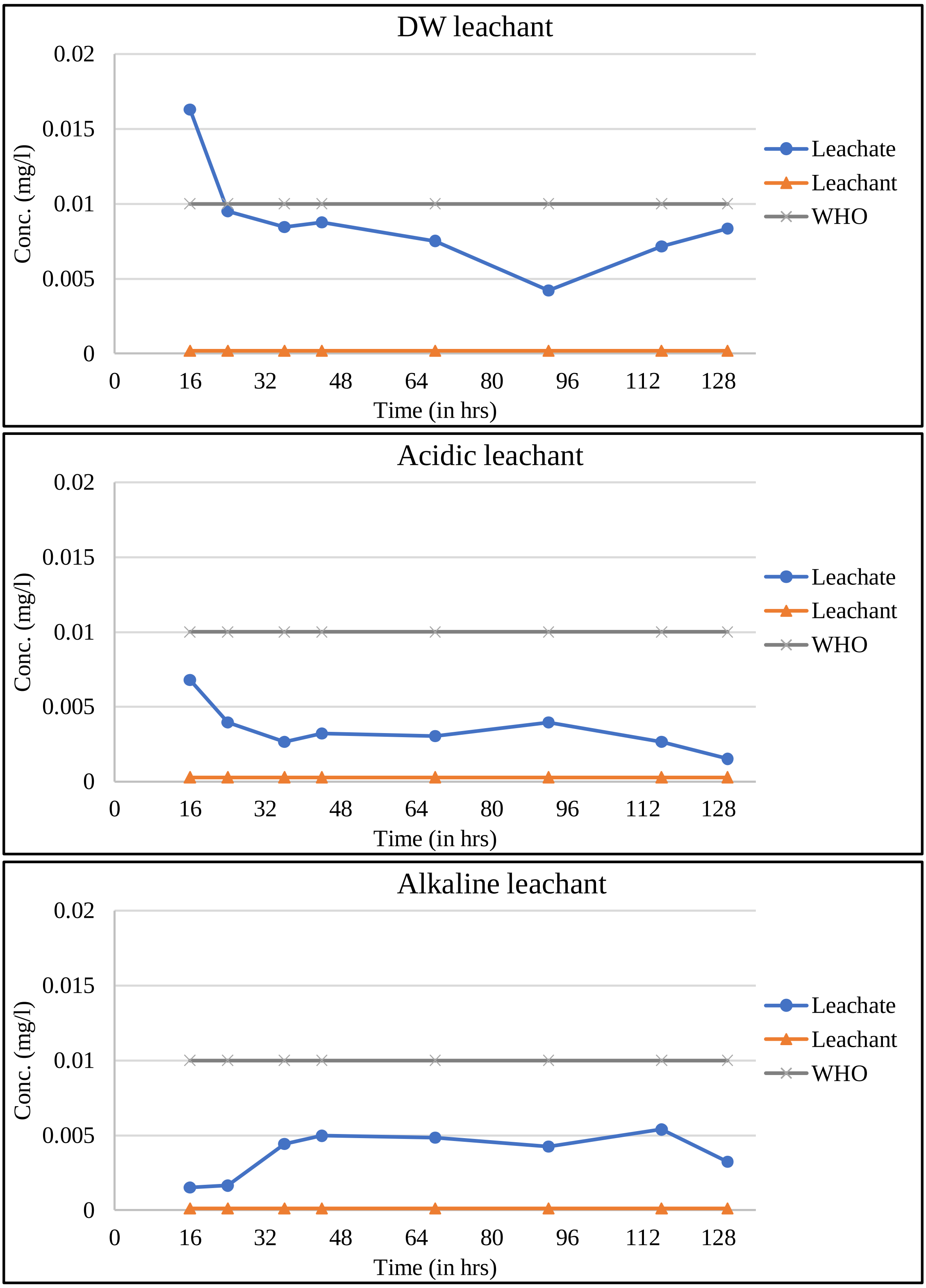


**Fig. 4.43** As concentration in column leaching results for different types of leachant

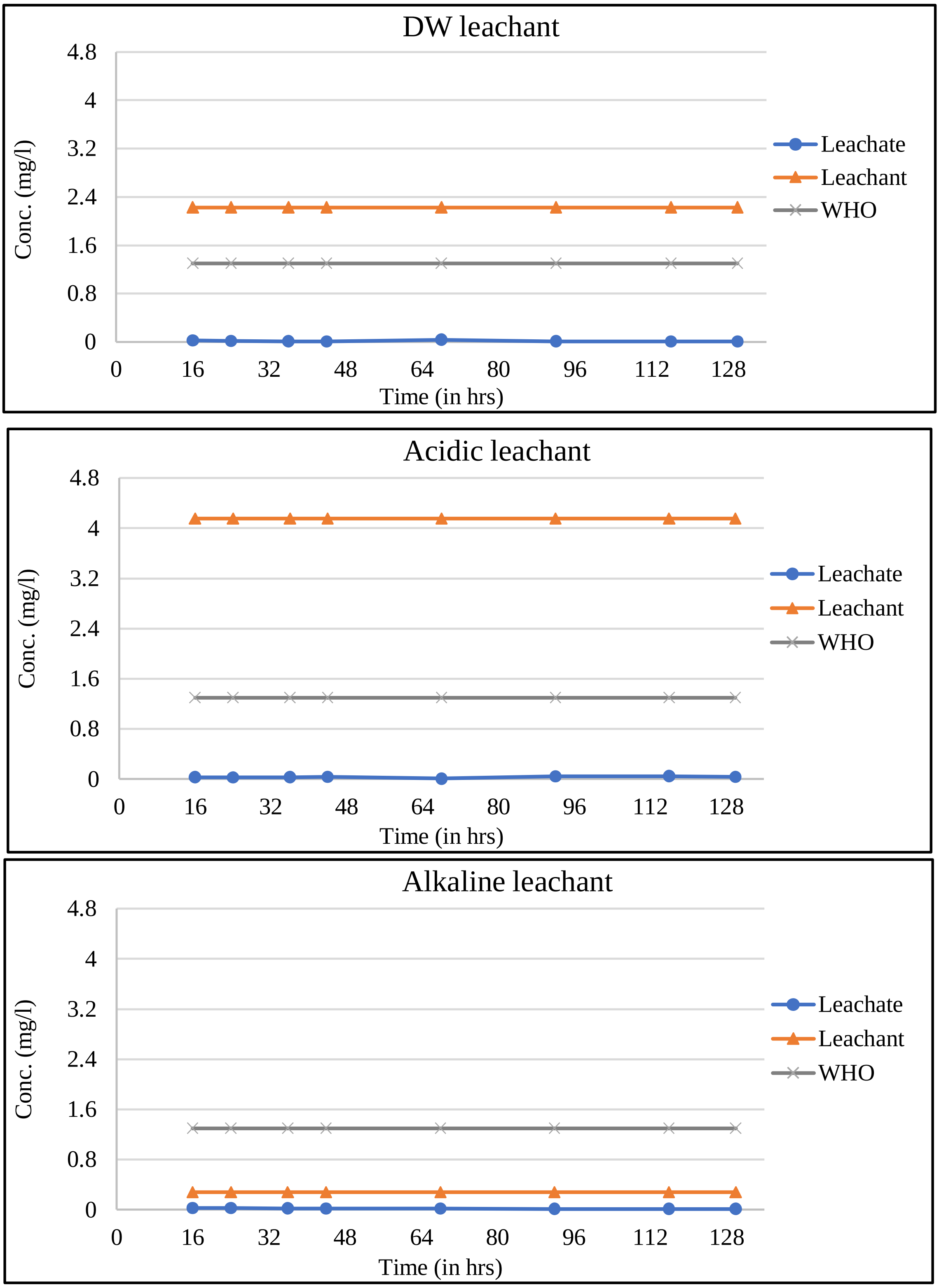


**Fig. 4.44** Ba concentration in column leaching results for different types of leachant

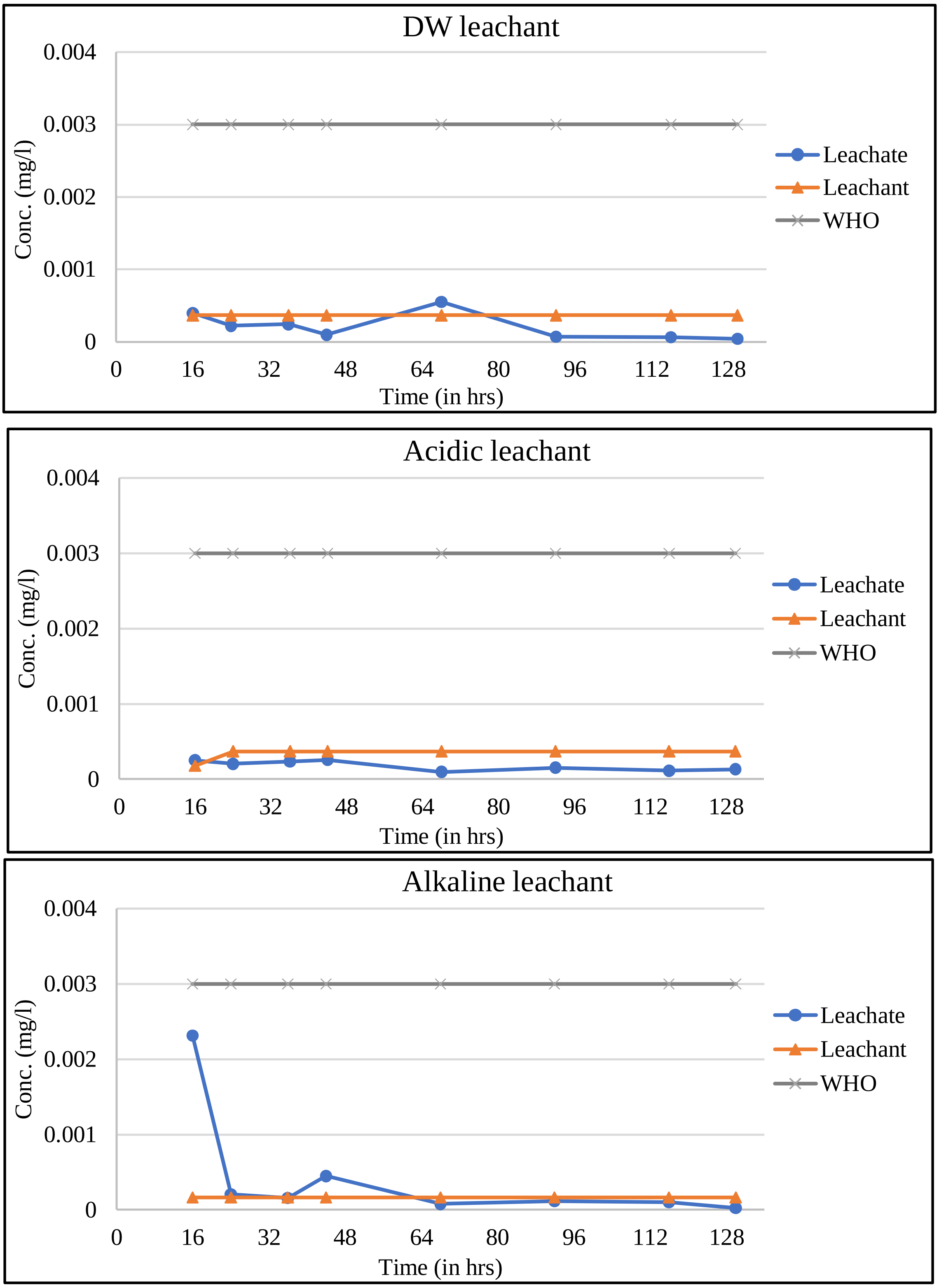


**Fig. 4.45** Cd concentration in column leaching results for different types of leachant

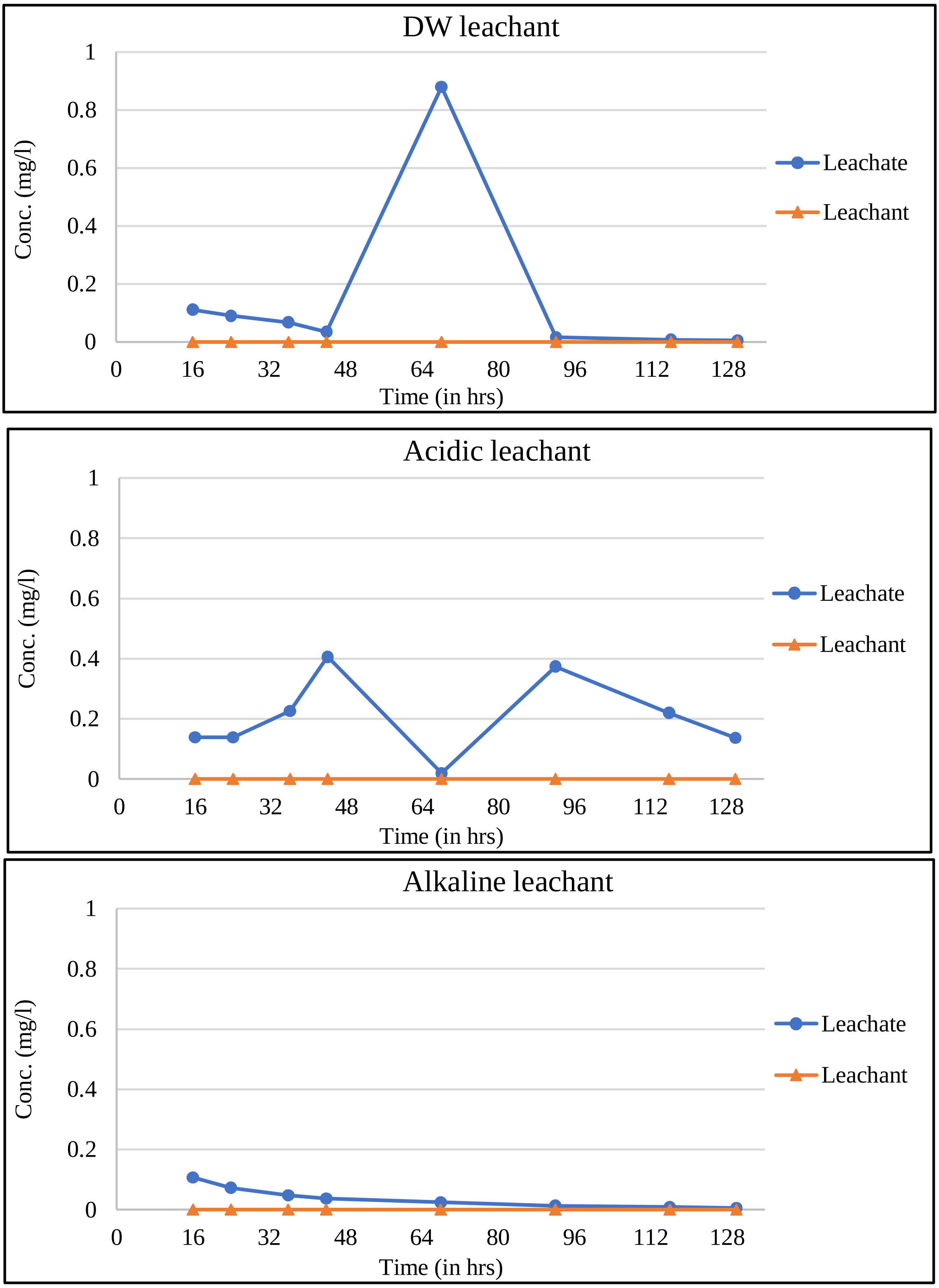


**Fig. 4.46** Co concentration in column leaching results for different types of leachant

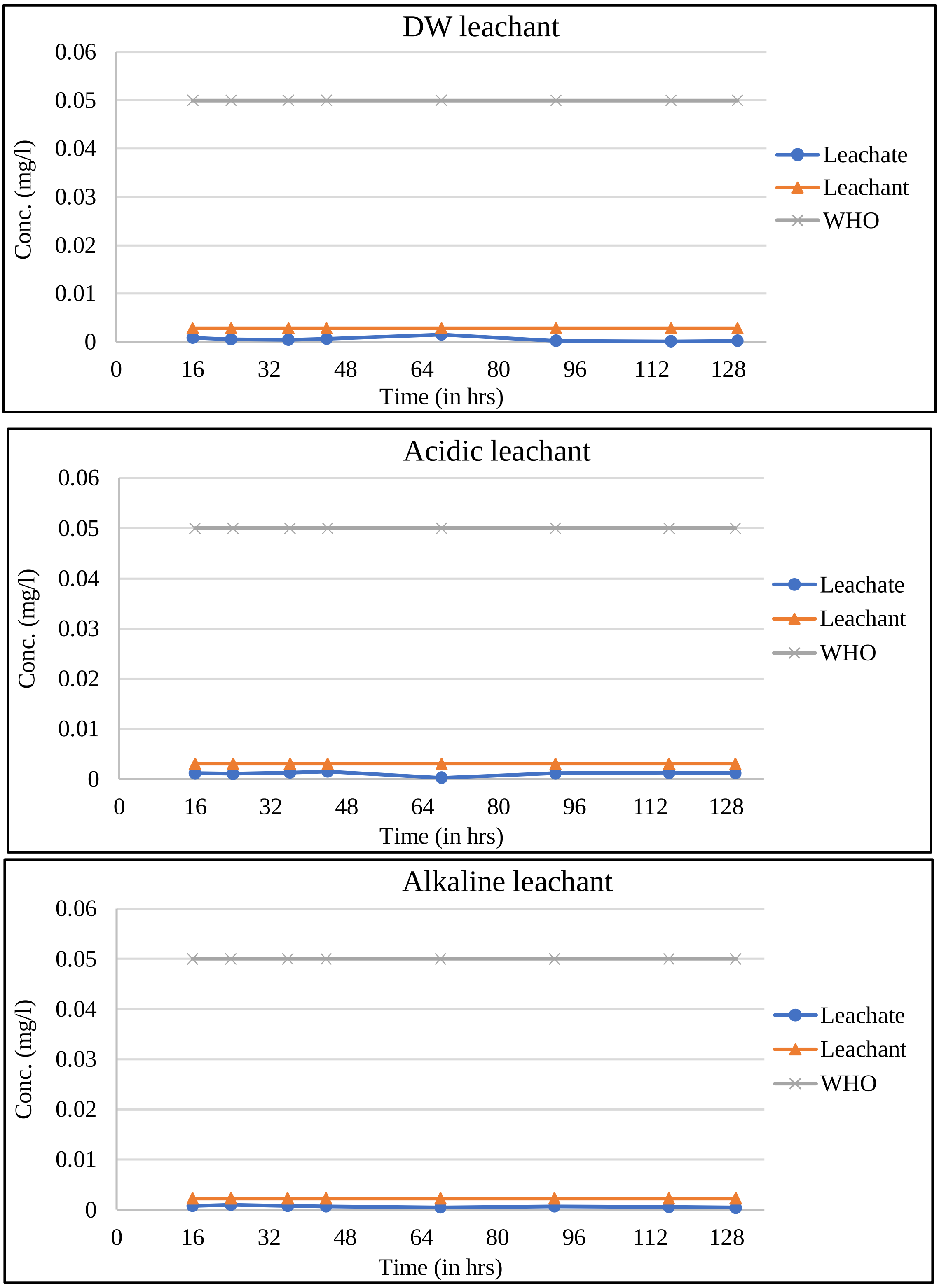


**Fig. 4.47** Cr concentration in column leaching results for different types of leachant

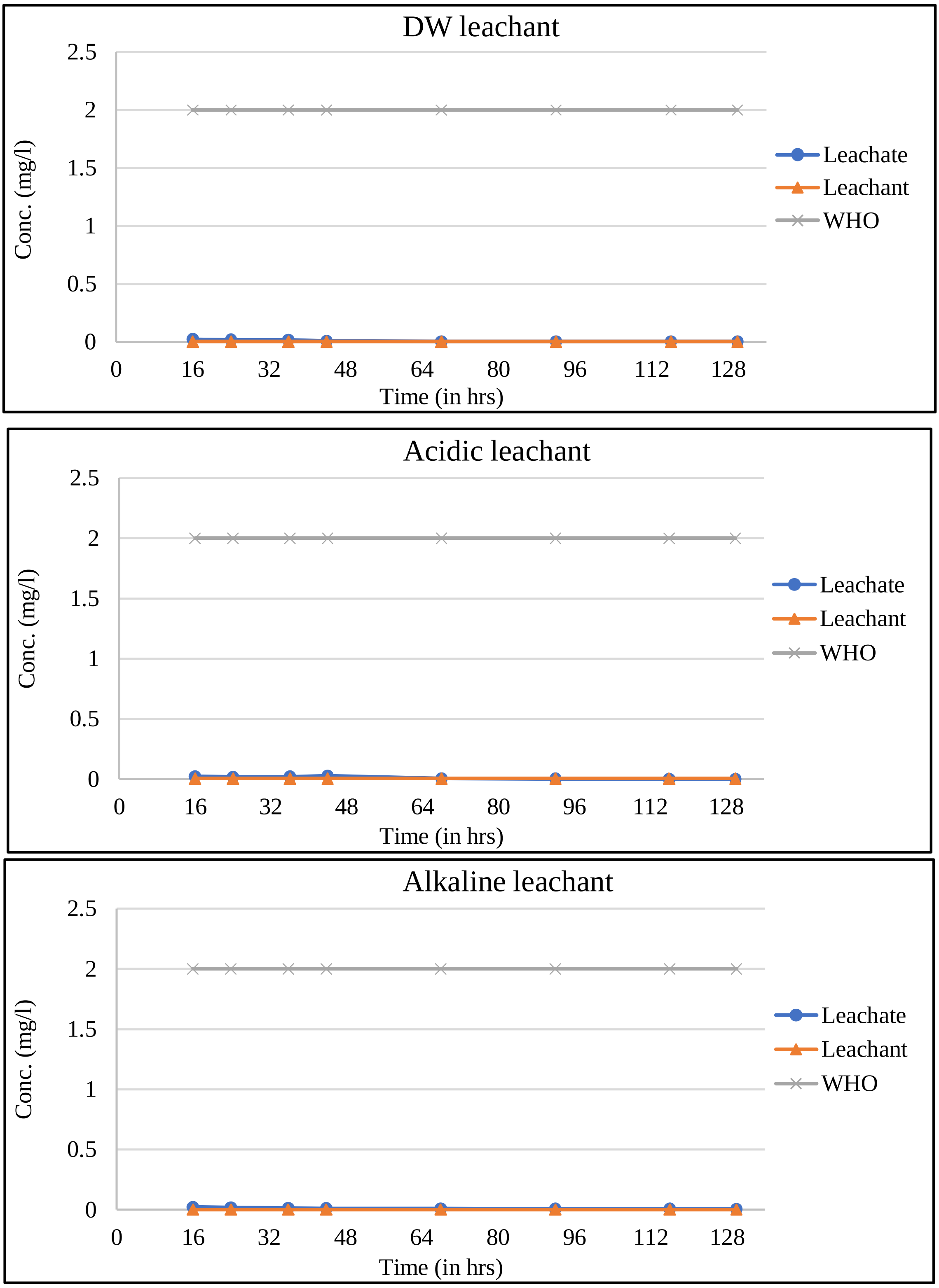


**Fig. 4.48** Cu concentration in column leaching results for different types of leachant

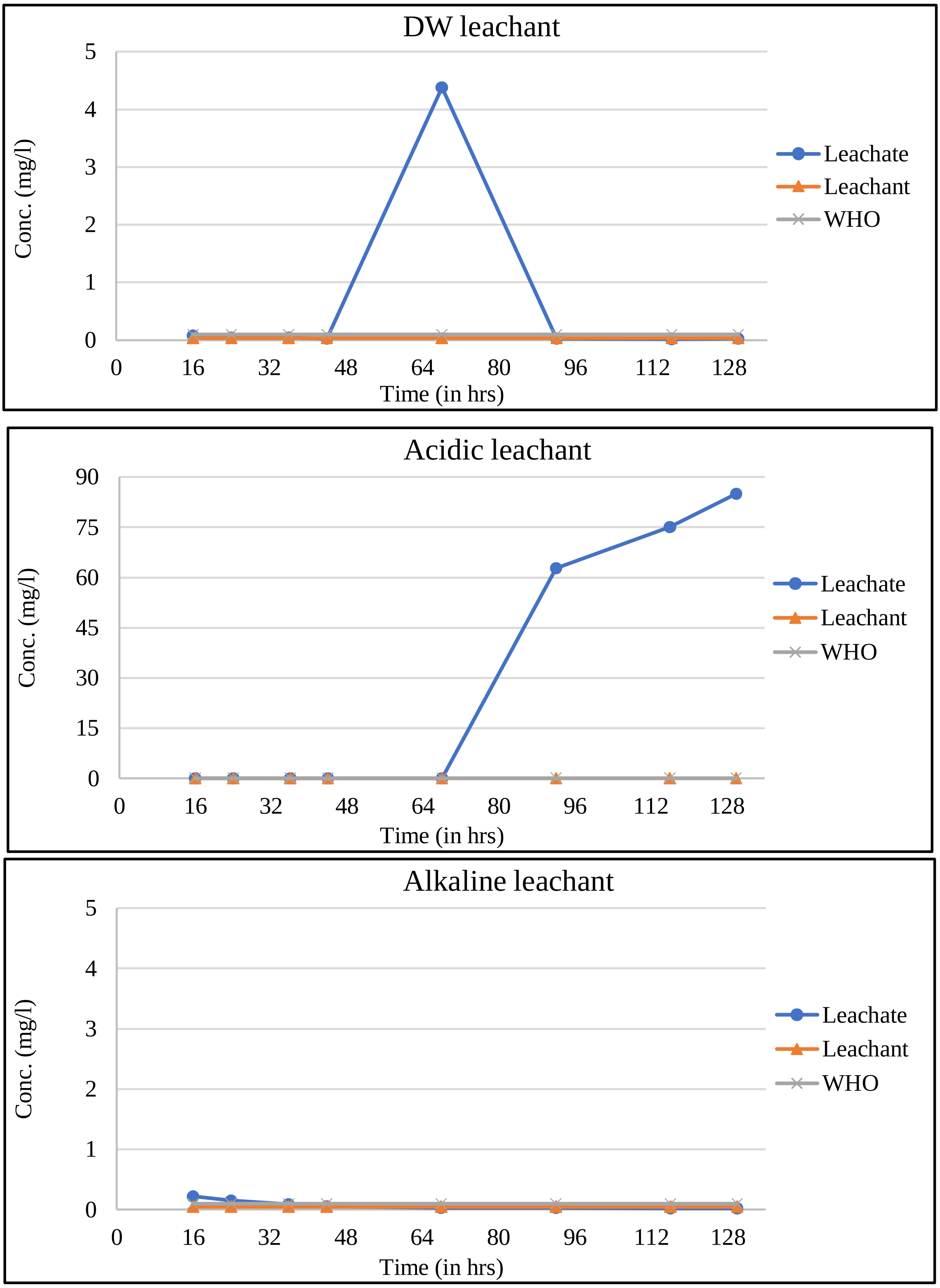


**Fig. 4.49** Fe concentration in column leaching results for different types of leachant

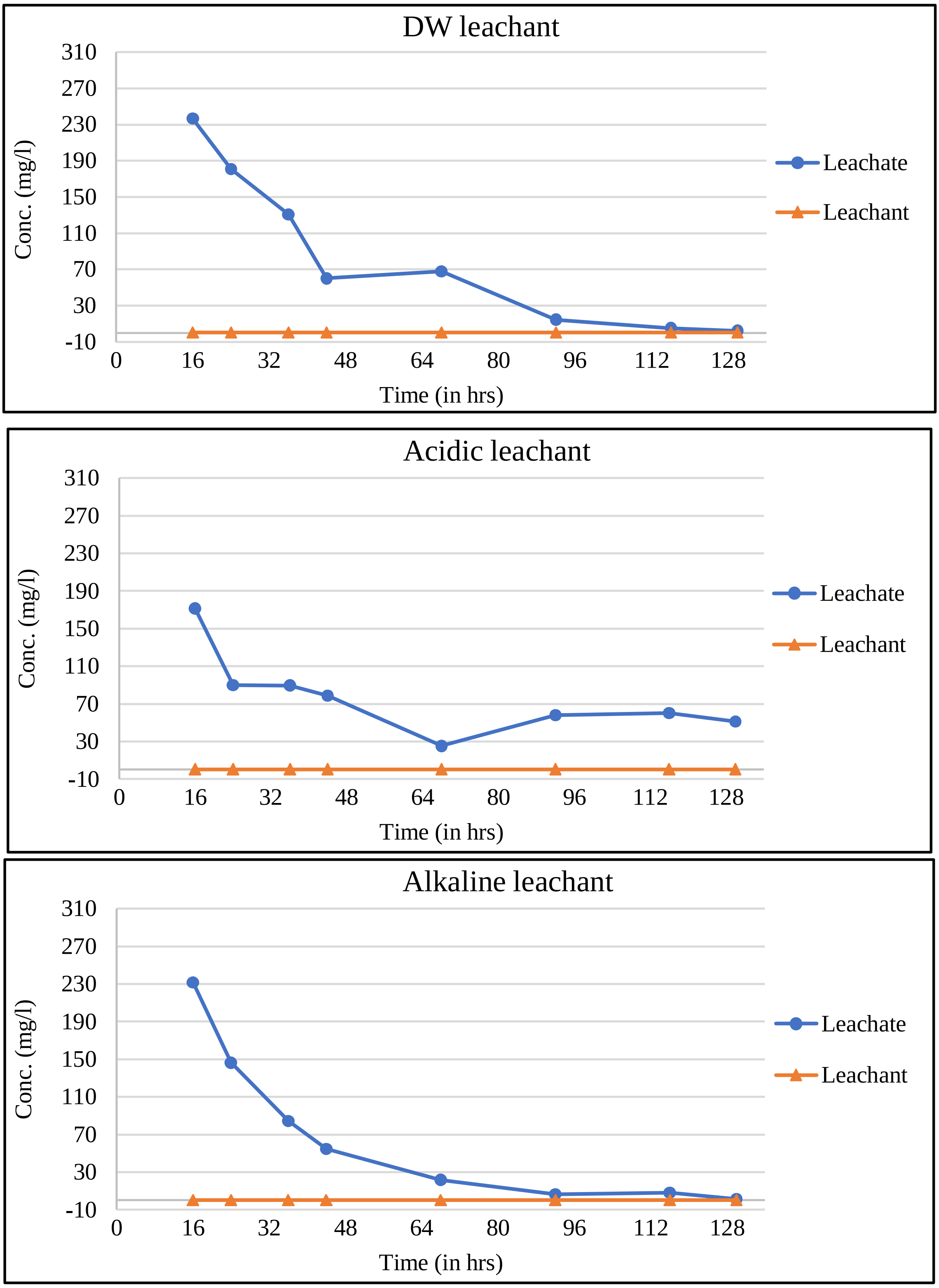


**Fig. 4.50** Mg concentration in column leaching results for different types of leachant

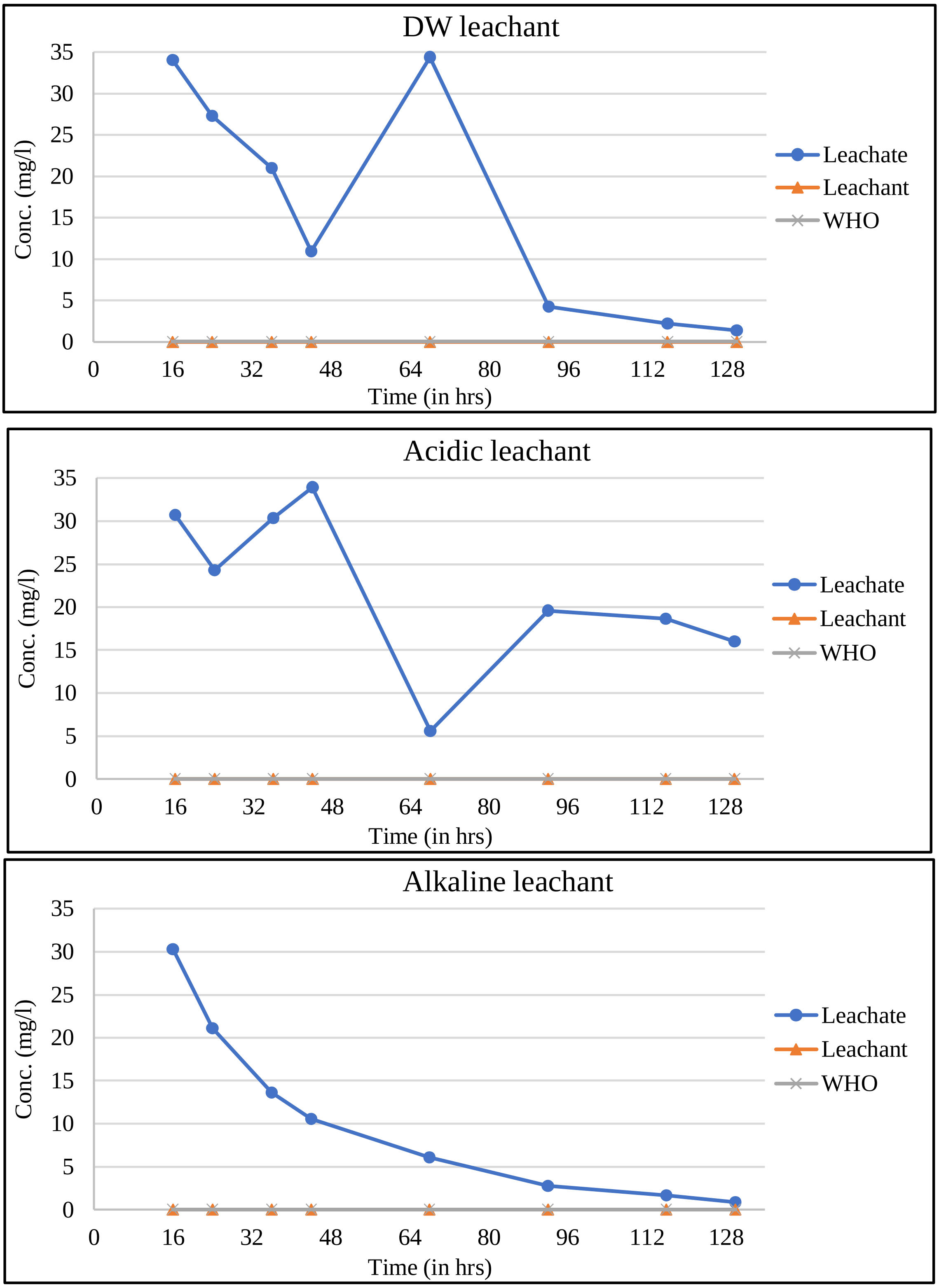


**Fig. 4.51** Mn concentration in column leaching results for different types of leachant

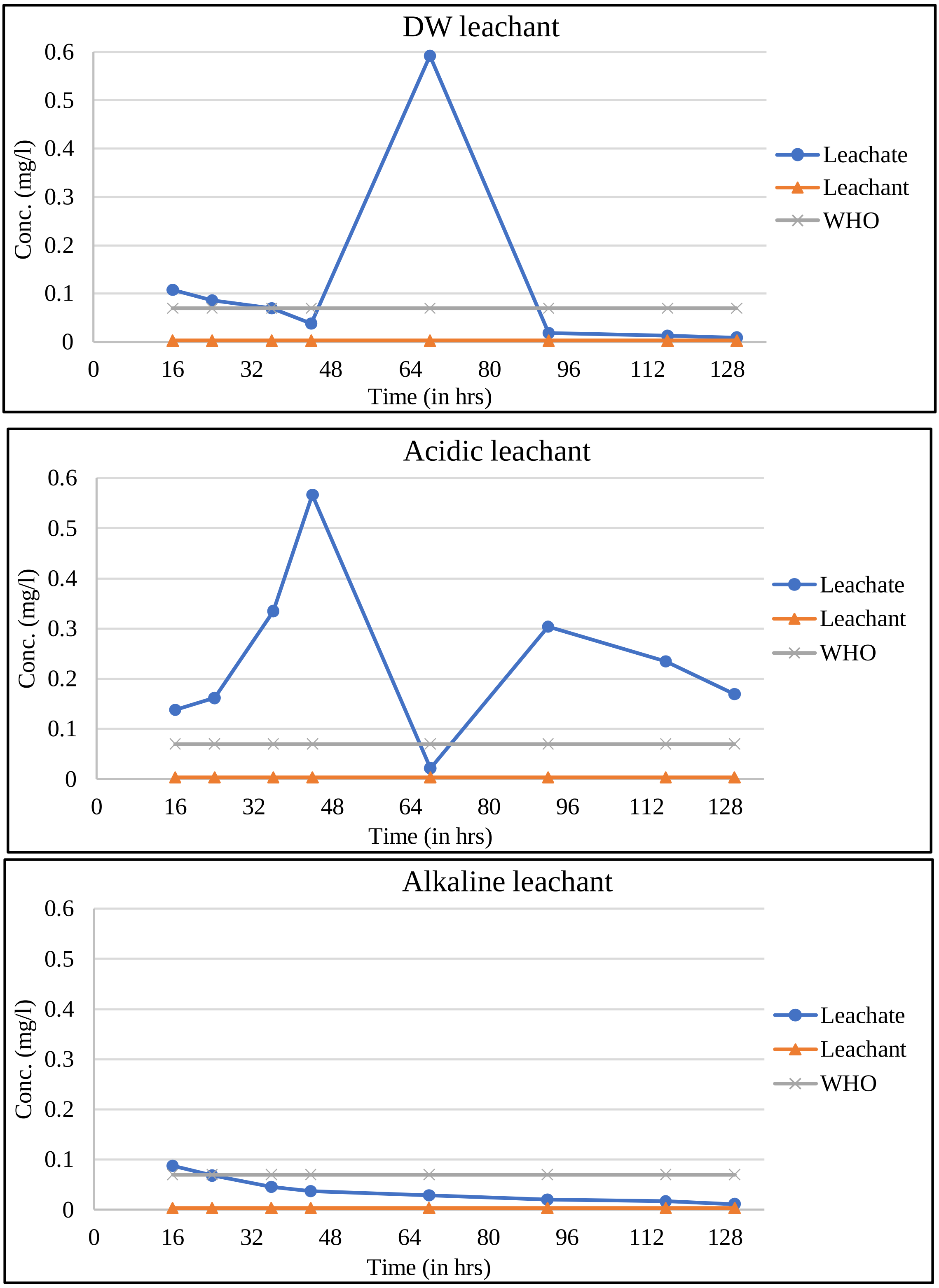


**Fig. 4.52** Ni concentration in column leaching results for different types of leachant

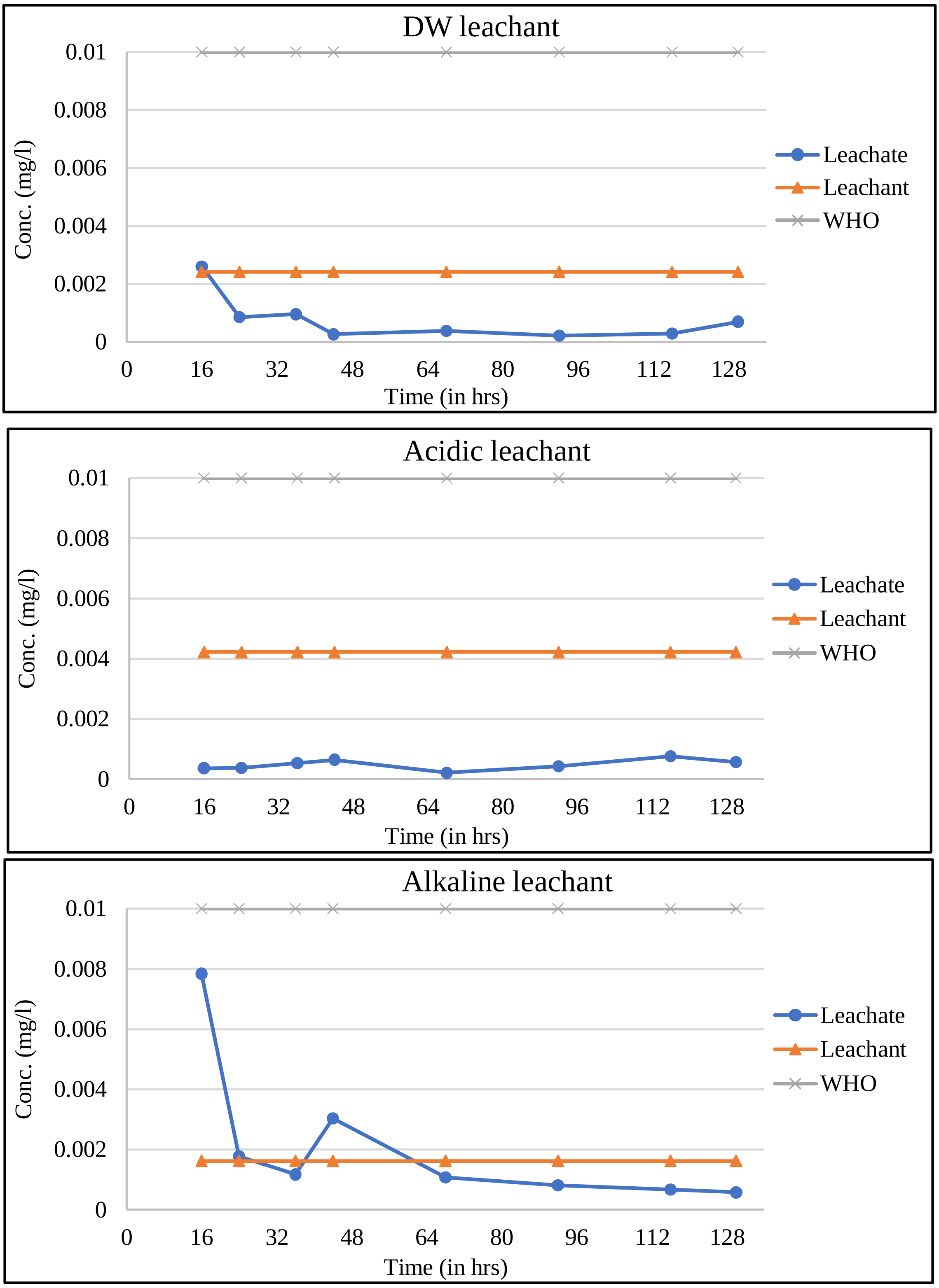


**Fig. 4.53** Pb concentration in column leaching results for different types of leachant

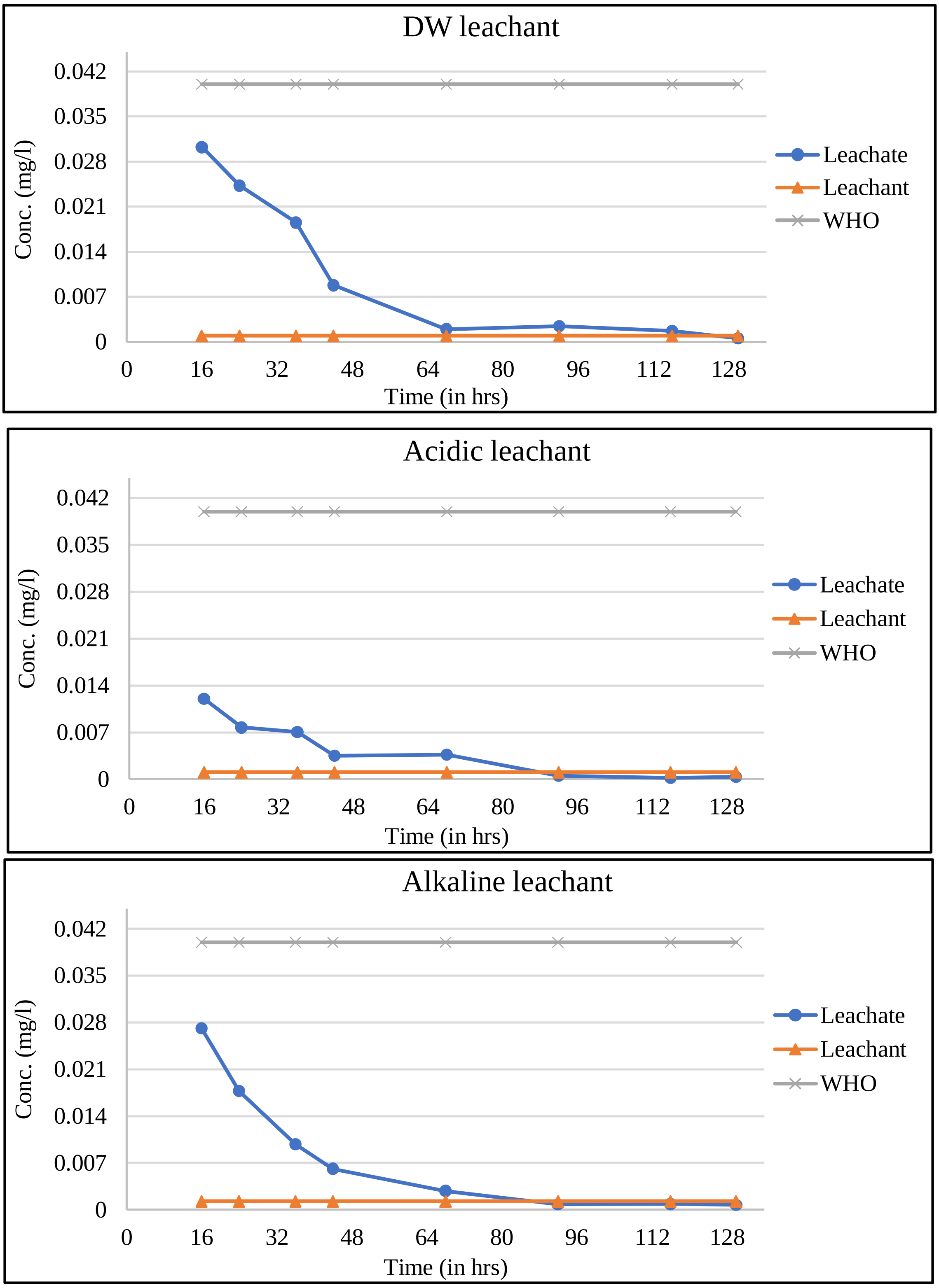


**Fig. 4.54** Se concentration in column leaching results for different types of leachant

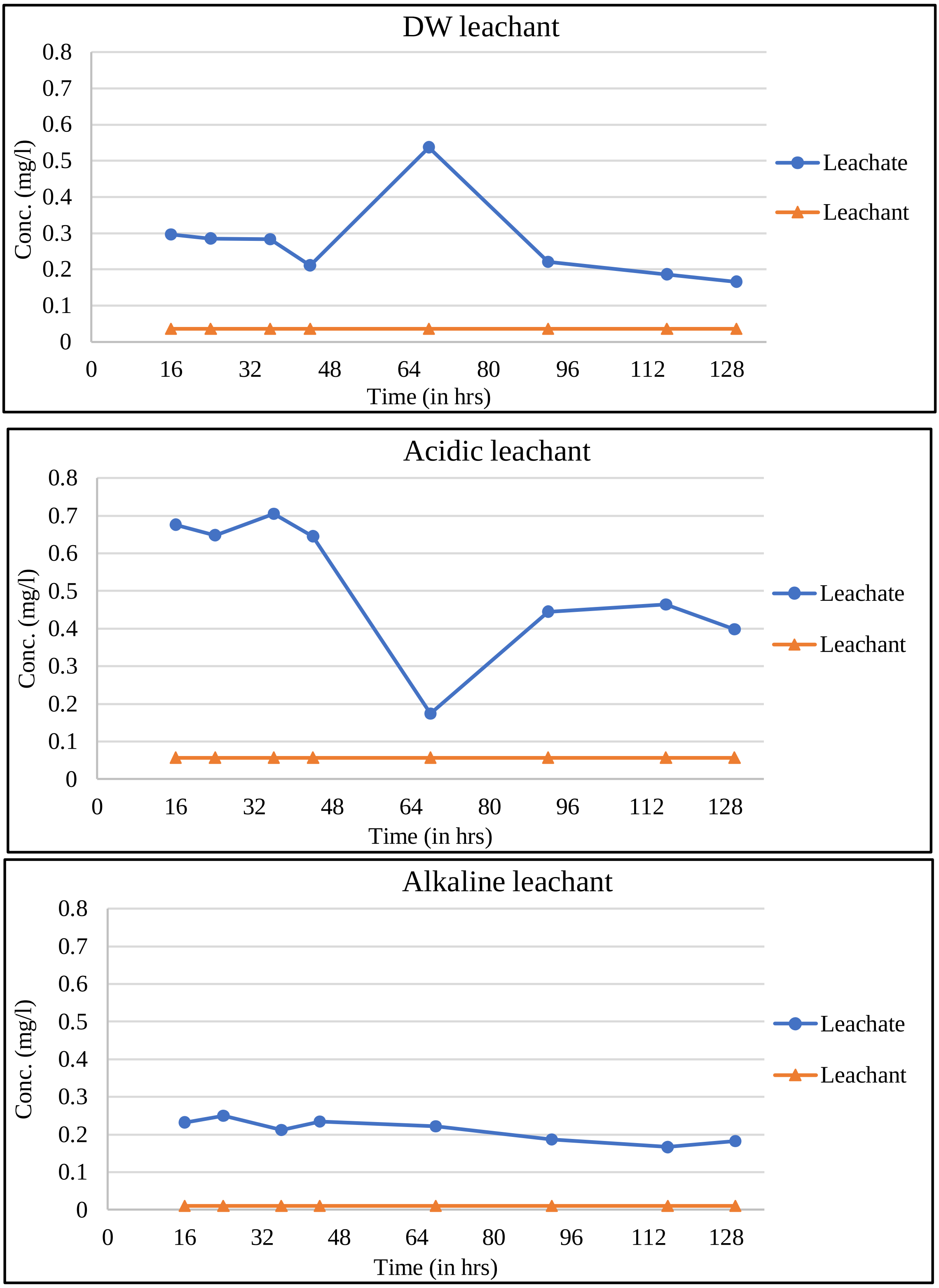


**Fig. 4.55** Sr concentration in column leaching results for different types of leachant

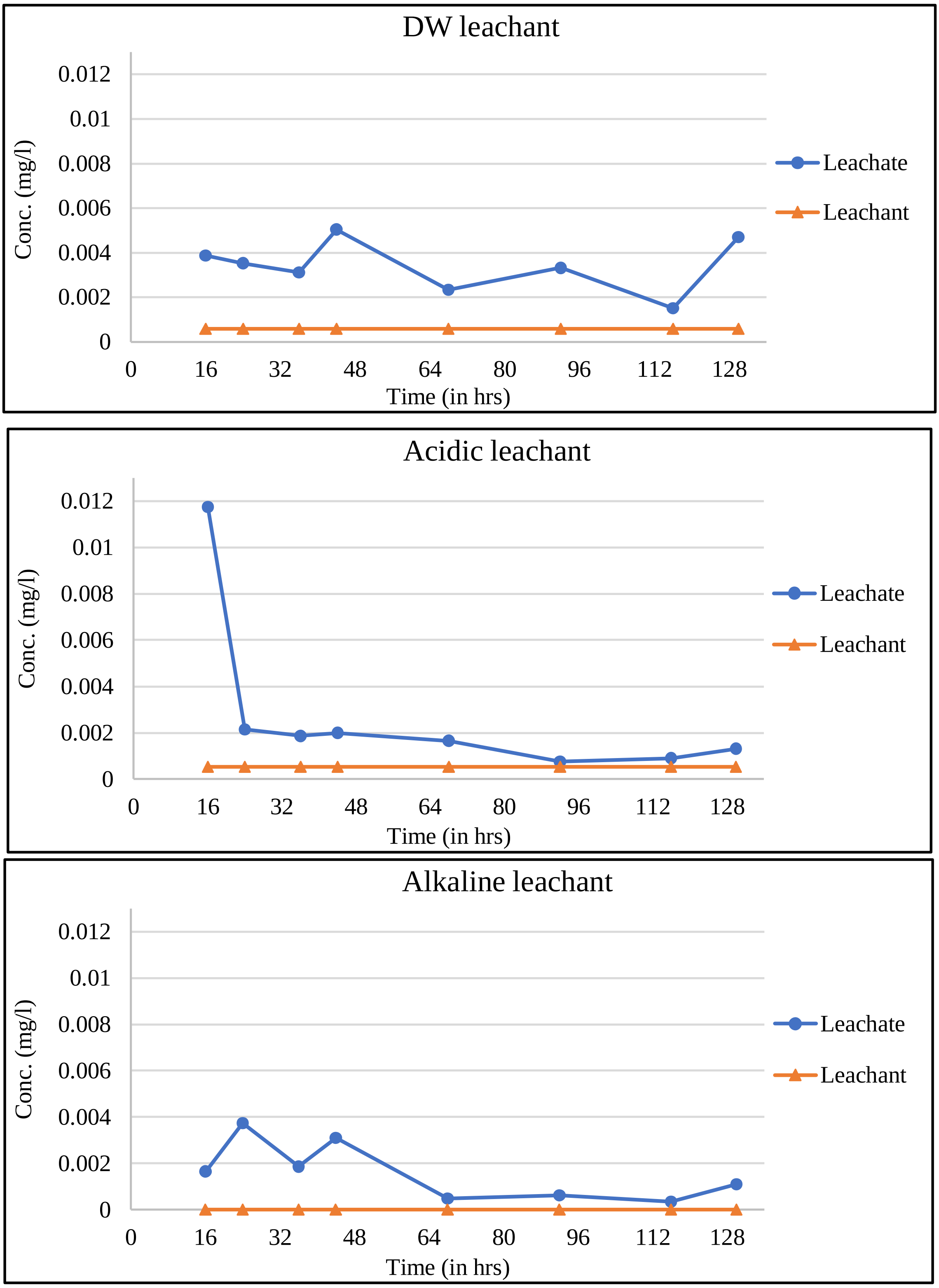


**Fig. 4.56** Ti concentration in column leaching results for different types of leachant

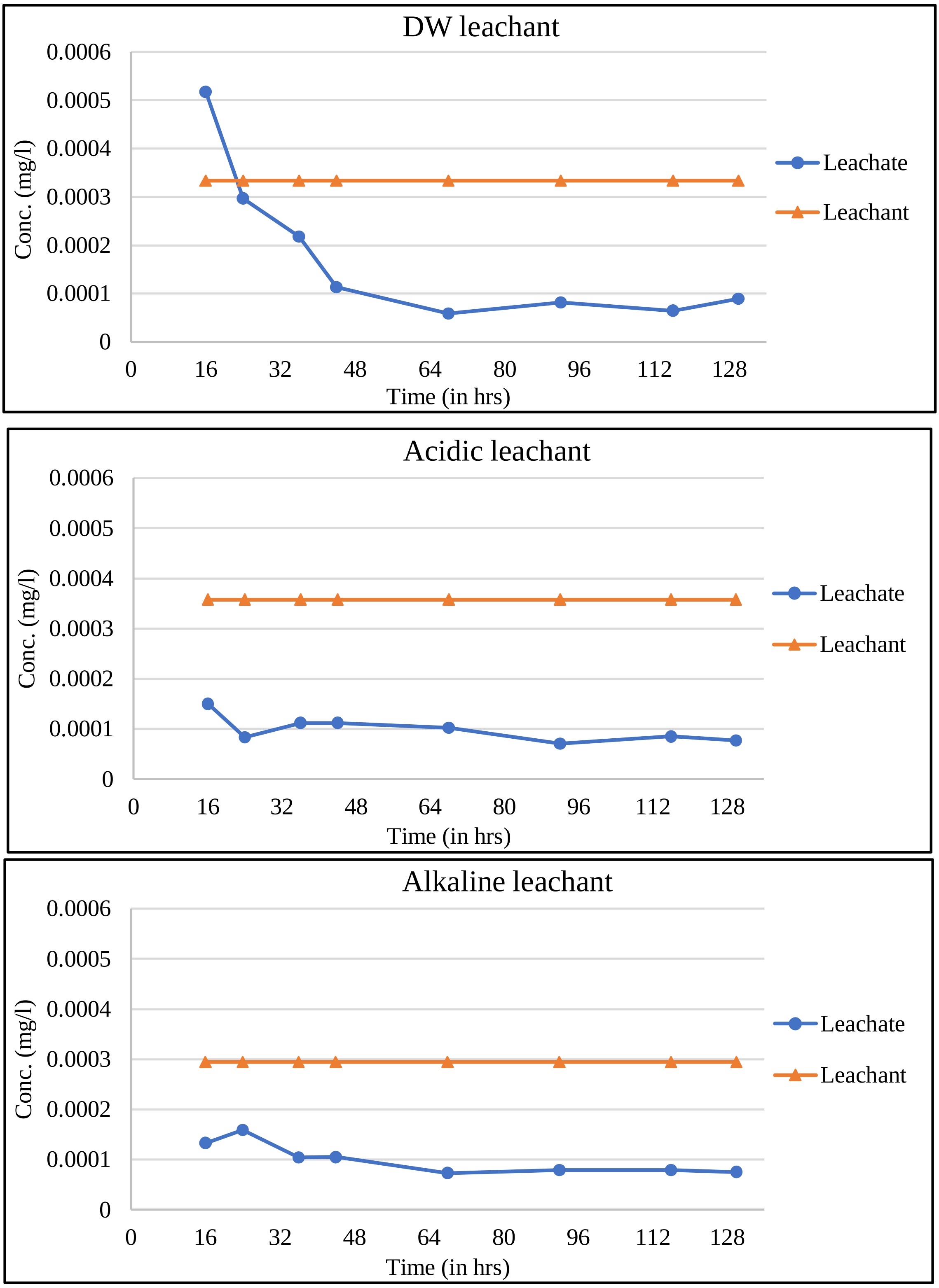


**Fig. 4.57** V concentration in column leaching results for different types of leachant

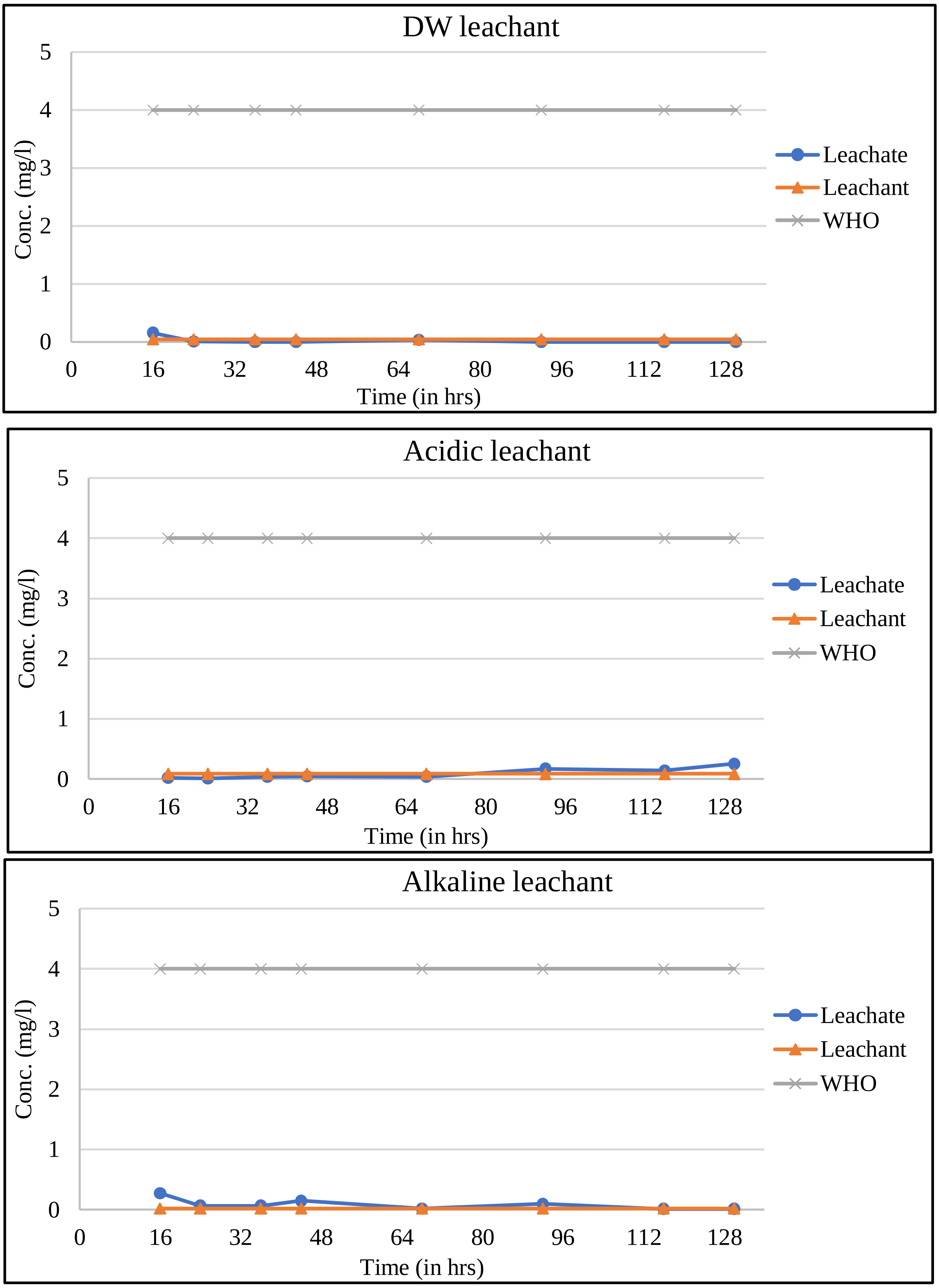


**Fig. 4.58** Zn concentration in column leaching results for different types of leachant

### 4.4.4 Groundwater analysis results

*Near Khetri copper tailing pond:*

Ten groundwater sampling sites were chosen, and sampling was done nearby copper tailings pond located in Khetri. The results of the analyzed samples are presented in Table 4.4. Value of Al is below the WHO standards, but it is about 33 % (in S-1 and S-8) to 333 % (in S-9) higher in the samples except for S-5 which is below the prescribed Indian standards. Ba is below the both WHO and Indian standard permissible guidelines. For Ca the value is above the Indian standards for all the locations from 116% higher at site S-7 to 964% higher at sampling location S-2. The Cu concentration is well below WHO guidelines. However, from Indian Standards, its values is 20% (in S-5) to 220% higher than the guidelines. Fe is very much higher in than the standards in all the groundwater samples. It is 70% higher in site S-2 to 13270% greater in sampling sites S-7. Site S-5 and S-6 are also having much higher (11760% and 9670% respectively) concentration of Fe than the standards. Mn is exceeded marginally (0.02 mg/L) to the WHO standards in sampling locations S-6.

*Near Suratgarh thermal power plant:*

The concentration range of different trace elements in groundwater near SSTPP is shown in Table 4.5 at 8 different locations. The concentration of Zn, As, Cu, Ni, Pb, Ca, and Mg is well below the standards prescribed by WHO and Bureau of Indian Standards (IS 10500:2012). Values of Cd, Cr, and Mn are slightly lower than the prescribed WHO standards. The concentration of Al is also below the prescribed limit of IS 10500:2012. Only Fe and Se concentrations in groundwater are alarming. The concentrations of Fe are more than (up to 400%) the standards in some samples and the case of Se, in some samples, it is up to 0.03 mg /L higher than the standards.

**Table 4.4** Heavy Metal Concentration in groundwater samples near copper tailings pond located in Khetri (mg/L)

| | S-1 | S-2 | S-3 | S-4 | S-5 | S-6 | S-7 | S-8 | S-9 | S-10 | WHO Limit | IS 10500:2012 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Al** | 0.04 | 0.09 | 0.05 | 0.05 | 0.02 | 0.05 | 0.08 | 0.04 | 0.13 | 0.07 | 0.1 | 0.03 |
| **Ba** | 0.07 | 0.05 | 0.07 | 0.14 | 0.08 | 0.03 | 0.03 | 0.07 | 0.10 | 0.10 | 1.3 | 0.7 |
| **Ca** | 379.73 | 798.15 | 200.08 | 298.22 | 284.20 | 541.72 | 162.28 | 236.47 | 360.17 | 209.60 | - | 75 |
| **Cu** | 0.05 | 0.05 | 0.10 | 0.09 | 0.06 | 0.08 | 0.16 | 0.05 | 0.08 | 0.05 | 2 | 0.05 |
| **Fe** | 0.17 | 0.90 | 4.05 | 1.37 | 11.86 | 9.77 | 13.37 | 0.37 | 3.12 | 0.44 | 0.1 | 0.1 |
| **Mg** | 75.82 | 340.77 | 48.30 | 68.58 | 66.85 | 277.64 | 34.53 | 58.19 | 83.07 | 52.33 | - | 30 |
| **Mn** | 0.05 | ND | 0.04 | 0.04 | 0.05 | 0.07 | 0.05 | 0.03 | 0.04 | 0.02 | 0.05 | 0.1 |
| **Na** | 325.66 | 324.12 | 78.42 | 166.29 | 623.63 | 278.53 | 257.46 | 207.37 | 85.33 | 185.23 | - | - |
| **Sr** | 1.44 | 4.72 | 0.99 | 1.47 | 1.84 | 2.22 | 0.89 | 1.08 | 1.21 | 1.18 | - | - |
| **V** | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | - | - |
| **Zn** | 0.17 | 3.90 | 1.32 | 3.80 | 2.95 | 0.13 | 2.92 | 0.22 | 2.35 | 0.32 | 4 | 5 |

**Table 4.5** Heavy metal Concentration in groundwater samples collected from the nearby FA dumping site

| Elements | Concentration range (mg/L) | Desirable drinking water limit (mg/L) | |
|---|---|---|---|
| | | WHO | IS 10500:2012 |
| Al | 0.001-0.015 | 0.1 | 0.03 |
| As | 0.001-0.042 | 0.01 | 0.01 |
| Ca | 17.4-85.6 | | 75 |
| Cd | <0.002 | 0.003 | 0.003 |
| Co | 0-0.001 | - | - |
| Cr | 0.001-0.018 | 0.05 | 0.05 |
| Cu | 0.001-0.038 | 2 | 0.05 |
| Fe | 0.301-1.545 | 0.1 | 0.3 |
| Mg | 17.5-82.6 | | 30 |
| Mn | 0-0.013 | 0.05 | 0.1 |
| Ni | 0-0.001 | 0.07 | 0.02 |
| Pb | <0.002 | 0.01 | 0.01 |
| Se | 0-0.077 | 0.04 | 0.01 |
| Si | 1.6-2.4 | - | - |
| Sr | 0.878-4.087 | - | - |
| Ti | 0.023-0.188 | - | - |
| V | 0.010-0.325 | - | - |
| Zn | 0.002-0.042 | 4 | 5 |

## 4.5 Summary

The current chapter focuses on the possible polluting effects on surrounding due to leaching process associated with FA and CT waste materials. A detail of leaching phenomena, laboratory leaching tests, and their significance are presented in earlier sections of this chapter. The ecological impact of waste disposal is detailed to understand the ill-effects on the environment. A sampling of FA and CT are done from the disposal sites. TCLP and ASTM batch leaching tests were conducted initially for FA-1 and FA-2 (Fresh and weathered fly ash) samples. The concentration of Ni is only higher for both FA-1 and FA-2 samples using TCLP tests.

ASTM and TCLP batch leaching tests of the combination of both FA and CT waste materials exhibit a higher concentration of As and Mn if the CT concentration is high. Regression analysis of bath leaching tests shows a positive correlation between pH and Co, Cu, Fe, Mg, and Mn. FA to CT ratio is negatively correlated with pH. The groundwater samples near the waste disposal sites were collected to perform analysis for the concentration of heavy metals.