JNCS
Journal of Nepal Chemical Society
March/April 2023, Vol. 43, No. 2, 46-52
ISSN: 2091-0304 (print)
DOI: https://doi.org/10.3126/jncs.v43i2.53340
RESEARCH ARTICLE

CHEMICAL AND INSTRUMENTAL ANALYSIS OF LIMESTONE AND RED CLAY FROM MAKWANPUR DISTRICT

Rupesh Kumar Dubey, Bishan Datt Bhatt*

Department of Chemistry, Tri-Chandra Multiple Campus, Tribhuvan University, Kathmandu, Nepal

*Corresponding author: bdbhatta@gmail.com

Submitted: 10 Dec 2022, Revised: 10 Feb 2023, Accepted: 12 Feb 2023

ABSTRACT

Limestone and red clay are widely used in construction as primary raw materials since they are readily available and economically viable. The present work has been carried out primarily to explore the fresh reserves of acceptable raw materials in Makawanpur district for producing cement. Four limestone and four red clay samples were collected from different locations of Makwanpur district. The samples were analysed using chemical (titrimetric and gravimetric) and instrumental (wave dispersive X-ray fluoroscopy, WDXRF) methods. Chemical as well as instrumental methods were utilized not only to authenticate the results, but also to evaluate the merits of these methods. Loss on ignition (LOI), determined gravimetrically, ranged from 41.98 to 39.03% for limestone samples and from 9.24 to 7.82% for red clay samples. Chemical analysis of limestone samples revealed the presence of 40.72 to 48.53 % CaO, 0.97 to 1.96 % Fe_2O_3, 1.83 to 3.64 % Al_2O_3 and 5.69 to 12.84 % SiO_2. Chemical analysis of red clay revealed the presence of 2.26 to 3.27 % CaO, 9.54 to 14.20 % Fe_2O_3, 12.90 to 19.68 % Al_2O_3 and 46.70 to 61.50 % SiO_2. The WDXRF analysis of limestone revealed the presence of 39.37 to 50.46 % CaO, 0.8 to 2.29 % Fe_2O_3, 1.34 to 3.01 % Al_2O_3 and 4.75 to 17.03 % SiO_2. The WDXRF analysis of red clay revealed the presence of 1.98 to 3.59 % CaO, 9.89 to 13.96 % Fe_2O_3, 12.45 to 19.82 % Al_2O_3 and 47.62 to 60.94 % SiO_2.

The analysed compositions were found to lie within the range allowed by Nepal Bureau of Standards and Metrology (NBSM) for the manufacture of high-quality cement. The results from the chemical methods were found to be in good agreement with the results from the instrumental method. This research is expected to contribute to the cement industry not only by providing an insight into raw material compatibility but also by evaluating the merits of these methods.

Keywords: *Cement, Limestone, Loss on ignition (LOI), Red clay, WDXRF*

INTRODUCTION

In the 21st century, cement has become one of the most important components of developmental work. This has created enormous strain on the raw material source, which is limited by nature, due to the establishment of new plants at a tremendous pace. Thus, there is a dire need to find an alternative raw material for the cement industries [1, 2].

Nepal, as a developing country, faces numerous challenges in ensuring steady progress in its basic development. Following the massive earthquakes that struck in April and May of 2015, in recent years, Nepal has seen an increase in the use of concrete [3]. Nepal's annual concrete demand increased progressively, from 4.54 million tons in 2014/15 to 4.81 million tons in 2015/16; 7 million tons in 2016/17; 8.12 million tons in 2017/18 and 9.05 million tons in 2018/19. The estimated annual demand for cement will be 20 million tons in 2023/24 and 25.88 million tons in 2024/25 [4].

Cement is a finely powdered substance that is plastic in nature. It has the ability to harden and set as a result of chemical reactions with water at room temperature. Limestone (the calcareous raw material for cement), which is found in large amounts in Nepal, is widely used as a key raw material in the manufacture of cement. Calcite is a mineral that makes up a sedimentary rock known as limestone. Calcium oxide (CaO), which is derived from naturally occurring calcium carbonate, is the main oxide used in cement. The secondary raw material is red clay (and argillaceous raw material for cement) [5, 6].

According to the report of the Department of Mines and Geology, Nepal possesses around 1.25 billion metric tons of the best cement-grade limestone deposits. 540 million tons of limestone deposits have been proven, while 110 million tons have been semi-proven, and there are possibilities of having an additional 420 million tons. Out of the total nation's area, limestone occupies about 7000 km^2.

Red clay is a special clay with a high liquid limit, a high porosity ratio, low compressibility, and other characteristics [7]. Red clay is widely distributed in rainy areas of the *Chure* range in Nepal. Red clay is used in the cement industry to help with strength and setting. It is commonly used in the cement industry for silicon, aluminium, and iron [8, 9]. Different locations in many districts contain good-quality red clay, which is used in cement industries.

Various methods have been used in the past for the quantitative analysis of one or more components of limestone and red clay. These methods include gravimetry, atomic absorption spectroscopy (AAS), UV/Visible Spectrophotometry, scanning electron microscopy (SEM/EDS) in combination with X-ray analysis and X-ray powder diffraction (XRD) techniques [6, 10, 11].

In the past, one or more separate methods of analysing raw materials were utilized. As far as the authors' current knowledge is concerned, a comprehensive study of chemical and instrumental methods has not been reported. The present work has been carried out to explore fresh reserves of limestone and red clay at various locations in Makwanpur district. Chemical (titrimetric and gravimetric) as well as instrumental (wave dispersive X-ray fluoroscopy, WDXRF) methods have been utilized to authenticate the results. These results have also been utilized to evaluate the merits of these methods. The present study is expected to contribute to the cement industry by providing an insight into the suitability of raw materials as well as an evaluation of the compatibility of chemical and instrumental methods.

MATERIALS AND METHODS

Instruments

The instruments used in the present study include

(a) Wavelength dispersive X-ray fluoroscope, WDXRF (S8 TIGER Series 2 of BRUKER Technology)

(b) Electrical muffle furnace (High temperature furnace LHT a/17D of Nabertherm)

Chemicals and reagents

All the reagents used were of analytical grade and free from moisture. The chemical used were from Merck and Thermo Fischer Scientific India Pvt Ltd Mumbai. Pyrex glassware were used. All the glassware was used after thorough cleaning with distilled water and drying in the oven.

Sample collection and preparation

For sample collection, four sites were selected within a 50 km^2 area of Makwanpur district of Nepal, covering *Budichour, Handikhola and Ratmate*. Samples of limestone and red clay were collected. These samples were hammered, and about 4 kg each of all these samples were placed in the properly tagged bags. They were labelled as LS1, LS2, LS3 and LS4 for limestone at collection site 1, 2, 3 & 4. Similarly, they were labelled RC1, RC2, RC3 and RC4 for red clay at collection sites 1, 2, 3 & 4. These samples were taken in the laboratory for the further treatment.

The samples were sundried before being crushed into bits as small as 2 mm in diameter, using a jaw crusher. The crushed samples were processed in a

Figure: *Samples of Red Clay*

Figure: *Samples of Limestone*

disk grinder using a vibrating machine in a ball mill. After quartering and coning the crushed sample, a representative portion was placed in labelled open glass bottles and baked at 110 °C for two hours until constant mass was obtained. After chilling in the desiccator, the bottles were correctly sealed. For further investigation, these moisture-free samples were employed [6, 12, 13].

Determination of loss on ignition (LOI)

Loss on ignition (LOI) was determined in all the samples to estimate the amounts of volatile impurities present in the samples under investigation. For this purpose, gravimetric method as described in the literature [14], was utilized.

Determination of percentage of CaO & Al_2O_3

Percentage of CaO in samples was determined by complexometric titration against ethylenediaminetetraacetic acid (EDTA) and the percentage of Al_2O_3 in samples was determined by double titration against zinc acetate, as described in the literature. [15].

Determination of percentage of Fe_2O_3

Percentage of Fe_2O_3 in samples was determined by dichromate titration as described in the literature [16]

Determination of percentage of SiO_2

Percentage of SiO_2 in samples was determined by gravimetric methodas described in the literature [12].

Instrumental analysis using Wave dispersive X-ray fluoroscopy (WDXRF)

WDXRF uses crystals to disperse the fluorescence spectrum into individual wavelengths of each element, providing high resolution and low background spectra for accurate determination of elemental concentrations. Crystal types used in WDXRF include mineral, metallic, organic, and synthetic multilayers. Due to the high sensitivity and resolution for light element analysis, these synthetic thin film multilayer crystals have gained good popularity. The working principle of WDXRF is based on Bragg's law. Accordingly, when there is a constructive interference of the scattered x-rays, crystals will reflect x-rays of specific wavelengths and incident angles. By changing the angles of the crystal and the detector, keeping the position of the sample fixed, a specific wavelength can be measured. Only x-rays that satisfy Bragg's law are reflected. The samples were subjected to WDXRF analysis for the determination of percentage CaO, Al_2O_3, Fe_2O_3 and SiO_2.

Table 1: *Percentage loss on ignition (LOI)in limestone & red clay samples*

	Samples							
	Limestone				Red Clay			
	LS1	LS2	LS3	LS4	RC1	RC2	RC3	RC4
LOI % by mass	39.03	41.72	40.23	41.98	7.82	9.24	8.76	8.26

* LS1, LS2, LS3 and LS4 are limestone samples collected at sites 1, 2, 3 and 4 respectively.

* RC1, RC2, RC3, RC4 are red clay samples collected at sites 1, 2, 3 and 4 respectively.

RESULTS AND DISCUSSION

Loss on ignition (LOI) of limestone & red clay

The gravimetric method was used to calculate the loss on ignition in limestone and red clay samples. The data obtained have been tabulated in Table 1 and graphically represented in Figure 1.

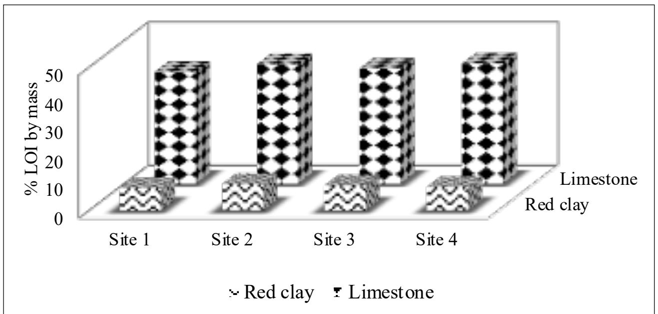

Figure 1. *Percentage loss on ignition in limestone and red clay samples*

Loss on ignition gives an idea about the total volatile content present in the sample. A higher value of LOI reflects the presence of a higher percentage of volatile content. The percent LOI in limestone and red clay were found to be 41.98 - 39.03 % and 9.24 - 7.82 %, respectively. The percentage LOI values were found to be nearly the same in the samples from all the sites. The highest LOI in limestone was found to be 41.98% and that for red clay was found to be 9.24 %. These results indicate the potential use of these raw materials for cement production.

Chemical analysis of limestone and red clay samples

The percentage by mass of CaO was determined by complexometric titration against ethylenediaminetetraacetic acid (EDTA). The percentage by mass of Fe_2O_3 was determined by dichromate titration. The percentage by mass of Al_2O_3 was determined by double titration method against zinc acetate. The percentage by mass of SiO_2 was determined gravimetrically. The results of chemical analysis in limestone samples have been tabulated in Table 2 and graphically represented in Figure 2.

Table 2: *Composition of limestone samplesas determined by chemical methods*

SAMPLES / COMPOSITION	LS1	LS2	LS3	LS4
% CaO	40.72	40.98	47.23	48.53
% Fe_2O_3	1.96	0.98	1.12	0.97
% SiO_2	12.84	8.78	5.86	5.69
% Al_2O_3	2.78	2.78	3.64	1.83

* LS1, LS2, LS3 and LS4 are limestone samples collected at sites 1, 2, 3 and 4 respectively.

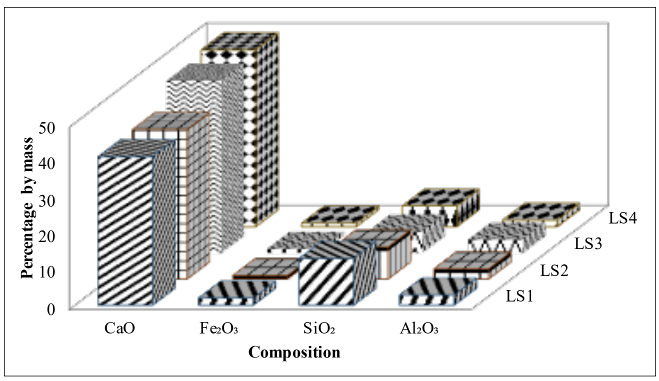

Figure 2: *Composition of limestone samples as determined by chemical methods*

The results of chemical analysis in red clay samples have been tabulated in Table 3 and graphically represented in Figure 3.

Table 3: *Composition of red clay samples as determined by chemical methods*

SAMPLES / COMPOSITION	RC1	RC2	RC3	RC4
% CaO	2.26	2.84	3.27	2.43
% Fe_2O_3	12.40	11.24	9.57	14.20
% SiO_2	61.50	59.24	54.28	46.70
% Al_2O_3	12.90	17.25	15.64	19.68

* RC1, RC2, RC3 and RC4 are red clay samples collected at sites 1, 2, 3 and 4 respectively

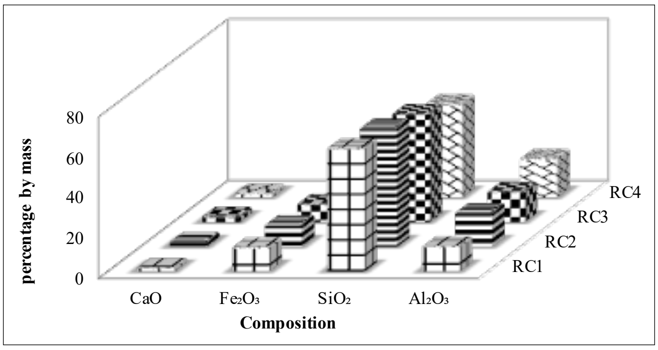

Figure 3: *Composition of red clay samples as determined by chemical methods*

These chemical methods of analysis in limestone samples revealed the presence of 40.72 to 48.53 % CaO, 0.97 to 1.96 % Fe_2O_3, 1.83 to 3.64 % Al_2O_3 and 5.69 to 12.84 % SiO_2. Similarly, chemical analysis in red clay samples revealed the presence of 2.26 to 3.27 % CaO, 9.54 to 14.20 % Fe_2O_3, 12.90 to 19.68 % Al_2O_3 and 46.70 to 61.50 % SiO_2. The compositions of the limestone and red clay samples from different locations have not been found to be much different. The compositions were found to be within the range allowed by Nepal Bureau of Standards and Metrology (NBSM) for the manufacture of high-quality cement.

Instrumental analysis of limestone and red clay samples

The percentage by mass of CaO, Fe_2O_3, Al_2O_3 and SiO_2 in all the limestone and red clay samples was also determined using wave dispersive X-ray fluoroscopy (WDXRF) method. The results of WDXRF analysis of limestone samples have been tabulated in Table 4 and graphically represented in Figure 4.

Table 4: *Composition of limestone samples as determined by WDXRF method*

SAMPLES / COMPOSITION	LS1	LS2	LS3	LS4
% CaO	39.37	44.25	50.07	50.46
% Fe_2O_3	2.29	1.17	0.86	0.8
% SiO_2	17.03	11.94	6.14	4.75
% Al_2O_3	3.01	2.23	1.67	1.34

* LS1, LS2, LS3 and LS4 are limestone samples collected at sites 1, 2, 3 and 4 respectively.

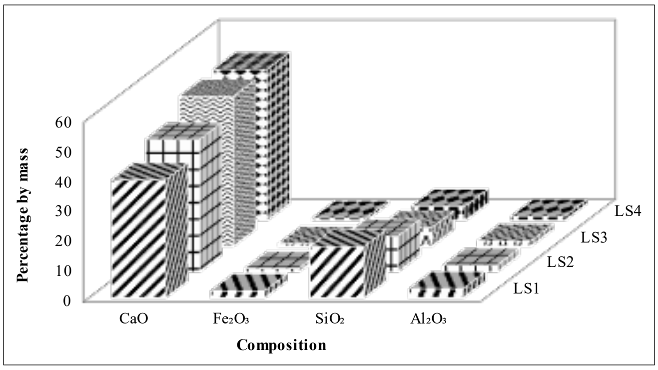

Figure 4: *Composition of limestone samples as determined by WDXRF method*

The results of WDXRF analysis in red clay samples have been tabulated in Table 5 and graphically represented in Figure 5.

Table 5: *Composition of red clay samples as determined by WDXRF method*

SAMPLES / COMPOUNDS	RC1	RC2	RC3	RC4
% CaO	1.98	3.02	3.59	2.87
% Fe_2O_3	12.81	11.02	9.89	13.96
% SiO_2	60.94	59.76	55.36	47.62
% Al_2O_3	12.45	17.13	15.21	19.82

* RC1, RC2, RC3 and RC4 are red clay samples collected at sites 1, 2, 3 and 4 respectively.

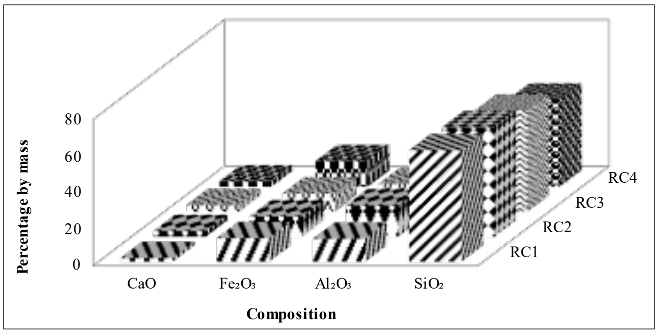

Figure 5: *Composition of red clay samples as determined by WDXRF method*

The WDXRF analysis of limestone revealed the presence of 39.37 to 50.46 % CaO, 0.8 to 2.29 % Fe_2O_3, 1.34 to 3.01 % Al_2O_3 and 4.75 to 17.03 % SiO_2. The WDXRF analysis of red clay revealed the presence of 1.98 to 3.59 % CaO, 9.89 to 13.96 % Fe_2O_3, 12.45 to 19.82 % Al_2O_3 and 47.62 to 60.94 % SiO_2.

The compositions of the limestone and red clay samples from different locations have not been found to be much different. The results obtained from currently used chemical methods as well as the WDXRF method were found to be almost similar to the results from other instrumental methods used by previous workers [6,10]. The results from the chemical methods were found to be in good agreement with the results from the instrumental method. These results show the potential of these raw materials for cement production. These results also indicate that the chemical and instrumental methods under investigation are compatible for the determination of the compositions of limestone and red clay as important raw materials for cement industry.

CONCLUSION

In the present work, limestone and red clay samples from different locations in Makwanpur district were analysed by chemical as well as instrumental methods. The low ignitability (LOI) values of limestone and red clay (up to 41.98% and 9.24%, respectively) indicate the presence of small amounts of volatiles in the samples. The high values of the oxides in limestone (up to

50.46 % CaO, 2.29 % Fe_2O_3, 3.64 % Al_2O_3 and 17.03 % SiO_2) and in red clay (up to 3.59 % CaO, 14.20 % Fe_2O_3, 19.82 % Al_2O_3 and 61.50 % SiO_2) vouch for the applicability of these raw materials for the production of high-quality cement.

In both methods, the compositions of the samples from the different locations were not found to be much different. The good agreement between the results from the chemical and instrumental methods of analysis indicated the compatibility of these methods. Moreover, the analysed composition was found to be within the range permitted by the Nepal Bureau of Standards and Metrology (NBSM) for the production of high-quality cement. These results indicate that the limestone and red clay of Makwanpur district are applicable for the production of high-quality cement. This research is expected to contribute to the cement industry not only by providing an insight into raw material compatibility but also by evaluating the merits of the chemical and instrumental methods for the analysis of raw materials for cement.

ACKNOWLEDGEMENTS

We would like to thank Ridhi Sidhi Cement Private Limited for providing their laboratory facilities for chemical as well as WDXRF analysis. We would like to express our gratitude to Dipendra Kumar (senior chemist at RSCPL) for his assistance and advice.

REFERENCES

1. A.K. Mishra, and U. Chaudhary, Assessment of Cement Handling Behavior for Selected Construction Sites of Bhatbhateni Supermarket, *Journal of Advanced Research in Construction and Urban Architecture*, 2018, 3(3), 1-11.
2. A.K. Mishra and A. Jha, Quality Assessment of Sarbottam Cement of Nepal, *International Journal of Operations Management and Services*, 2019, 9(1), 1-22.

3. D. Neupane, B. Sharma, A. Aryal, S. Acharya, M. Subedi, and B.GC,. Detailed Study of Cement Manufacturing Industry, *Ministry of Industry, Commerce, Supplies, Nepal*, 2019. https://www.doind.gov.np/detail/61. Retrieved on May 18, 2022.

4. Foreign Direct Investment in Cement Industry in Nepal a Study on Socio-economic Impact, *Nepal Rastra Bank*, 2020. https://www.nrb.org.np/contents/uploads/2021/05/2078.01.25-Final-Draft-of-Cement.pdf, Accessed on 22/04/2022.

5. N.U. Amin and K. Ali, Chemical analysis and Comparison of Ordinary Portland Cement of Khyber Pakhtoon Khwa Pakistan. *Chemical Engineering Research Bulletin*, 2010, 14(1), 45-49. (DOI: https://doi.org/10.3329/cerb.v14i1.4320)

6. K. Ali, N.U. Amin and T.M. Shah, Chemical Study of Limestone and Clay for Cement Manufacturing in Darukhula, Nizampur District, Nowshera, North West Frontier Province (N.W.F.P.), Pakistan. *Chinese Journal of Geochemistry*, 2008, 27(3), 242–248. (DOI: https://doi.org/10.1007/s11631-008-0242-8)

7. Y. Qi, M. Bai, H. Zhou, H. Shi, P. Li and B. He, Study on the Mechanical Properties of Red Clay under Drying-Wetting Cycles, *Advances in Materials Science and Engineering*, 2021, 2021, 1–16. (DOI: https://doi.org/10.1155/2021/8665167)

8. F. W. Clarke, The Composition of the Red Clay, *The Journal of Geology,* 1907, 15 (8), 783-789. https://www.jstor.org/stable/30067871

9. B. Velde, Uses of clays. In: Introduction to Clay Minerals, *Springer, Dordrecht*,1992, 164-176. (DOI: https://doi.org/10.1007/978-94-011-2368-6_5).

10. R.B. Gharti, D.K. Hitan, M. K. Prasad, and H.B. Oli, Chemical analysis of Limestone of Bojhe, Halesi-Tuwachung Municipality, for Industrial Applications. *Amrit Research Journal*, 2020, 1(1), 59–64. (DOI: https://doi.org/10.3126/arj.v1i1.32455)

11. A. I. Inegbenebor, A. O. Inegbenebor, R.C. Mordi, N. Kalada, A. Falomo, and P. Sanyaolu, Determination of the Chemical Compositions of Clay Deposits from Some Part of South West Nigeria for Industrial Applications, *International Journal of Applied Sciences and Biotechnology*, (2016), 4(1), 21–26. (DOI: https://doi.org/10.3126/ijasbt.v4i1.14214)

12. Methods of Sampling Dolomite, Limestone and Other Allied Materials, *Bureau of Indian Standards, New Delhi*, 1982, Reaffirmed 2003, 1-14.

13. G.H. Jeffery, J. Bassett, J. Mendham and R. C. Denney, Vogel's Textbook of Quantitative chemical analysis, 4th ed*., John Wiley & Sons Inc*., *New York*, 1989

14. Methods of chemical analysis of limestone, dolomite and allied materials-Part 1, Bureau of Indian standards, IS. 1760-1, 1991. https://law.resource.org/pub/in/bis/S10/is.1760.1.1991.pdf, Accessed on 22/04/2022.

15. Methods of chemical analysis of limestone, dolomite and allied materials- Part 3, Bureau of Indian standards,IS. 1760-3, 1991. https://law.resource.org/pub/in/bis/S10/is.1760.3.1992.pdf, Accessed on 22/04/2022.

16. Manual of Procedure for Chemical and Instrumental Analysis of Ores, Minerals, Ore Dressing Products and Environmental Samples, *Controller General Indian Bureau of Mines, NAGPUR*, February 2012. https://vdocuments.mx/manual-of-procedure-for-chemical-and-instrumental-analysis.html?page=1, Accessed on 22/04/2022.