INVESTIGATION OF FREE CALCIUM OXIDE IN PORTLAND CEMENT CLINKER

Otaqo'ziyev Akramjon Adaxamjonovich
Andijan State Technical Institute
ataqoziyev@gmail.com
Orazimbetova Guliston Jaksilikovna
Associate Professor,
Andijan State Technical Institute
gulistanorazimbetova0430@gmail.com
Xudayberdiyev Mahmudjon Qurbonovich
Andijan State Technical Institute
Teacher of the Department of General Technical Sciences
Qodirova Xurriyat Abobakir qizi
Andijan State Technical Institute
qodirovaxurriyat4@gmail.com

Abstract

Free calcium oxide (free CaO) is a critical quality parameter in Portland cement clinker. This study investigates the determination of free CaO in laboratory-prepared clinker samples using the ethylene glycol extraction method followed by titration with benzoic acid. Three clinker compositions were analyzed: limestone–slag–clay, limestone–slag, and limestone–clay–coal ash. The results demonstrate that raw mix composition significantly influences free lime content and clinker quality.

Keywords

Portland cement clinker; free CaO; ethylene glycol method; cement chemistry; clinker mineralogy

1. Introduction

Portland cement clinker is produced by sintering limestone, clay, and corrective materials at approximately 1450°C. It consists mainly of alite (C3S), belite (C2S), aluminate (C3A), and ferrite (C4AF). Clinker quality determines cement strength development, durability, and dimensional stability.

Free CaO represents unreacted lime remaining after clinkerization. Excess free lime may cause expansion and cracking in hardened cement. Therefore, accurate determination of free CaO is essential for quality control and research purposes. Portland cement clinker is the intermediate product obtained by sintering a precisely proportioned mixture of limestone, clay, and corrective materials at temperatures around 1450°C. It consists mainly of alite (C_3S), belite (C_2S), aluminate (C_3A), and ferrite (C_4AF) phases. Clinker plays a crucial role in cement production, as its mineralogical composition determines strength development, setting behavior, and durability.

Clinker is widely used in:

- Construction of buildings and infrastructure
- Hydraulic structures
- Road and bridge engineering
- Precast concrete production
- Oil well cementing applications

The quality of clinker directly affects cement performance. One of the most significant indicators of clinker quality is the amount of **free calcium oxide (free CaO)** remaining after the burning process.

Free CaO represents unreacted lime that did not combine with silica, alumina, and iron oxides during sintering. Excess free CaO may cause:

- Unsoundness and expansion
- Cracking in hardened cement
- Reduced durability

Therefore, accurate determination of free CaO is essential in clinker research and industrial quality control.

2. Materials and Methods

Why Determine Free CaO?

Free CaO indicates the completeness of clinker formation. During clinkerization, $CaCO_3$ decomposes:

$$CaCO_3 \rightarrow CaO + CO_2$$

The produced CaO reacts with SiO_2:

$$2CaO + SiO_2 \rightarrow C_2S$$

$$3CaO + SiO_2 \rightarrow C_3S$$

If burning conditions are insufficient (low temperature, short retention time, improper mix homogeneity), part of CaO remains unreacted.

Free CaO content typically should not exceed 1.5% in high-quality clinker.

Three clinker samples were prepared under laboratory kiln conditions at 1450°C.

Sample A: Limestone + Slag + Clay

Sample B: Limestone + Slag

Sample C: Limestone + Clay + Coal Ash

Free CaO was determined using the ethylene glycol extraction method. 1 g of finely ground clinker was mixed with 50 mL ethylene glycol and heated at 75°C for 30 minutes. The filtrate was titrated with standard benzoic acid solution.

2.1 Methods of Determination

Several researchers have contributed to free CaO determination methods:

R. H. Bogue — clinker phase chemistry, Lea & Parker — classical cement chemistry, Taylor — cement hydration and mineralogy, In Uzbekistan, cement research has been conducted at: Tashkent State Technical University, Institute of General and Inorganic Chemistry (Academy of Sciences of Uzbekistan) Uzbek researchers have focused on: Use of industrial waste (slag, coal ash), Optimization of raw mix composition, Clinker phase stability

2.2 Experimental Determination Method

In this study, the ethylene glycol extraction method was used.

Principle:

Free CaO reacts with ethylene glycol to form calcium glycolate:

$$CaO + HOCH_2CH_2OH \rightarrow Ca(C_2H_4O_2) + H_2O$$

The extracted solution is titrated using benzoic acid solution.

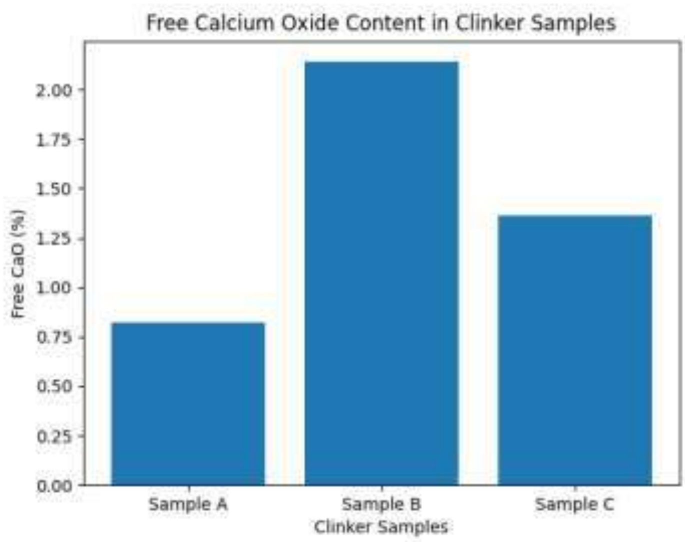
Procedure:

1. Finely grind clinker sample (≤ 90 µm).
2. Weigh 1.000 g sample.
3. Add 50 mL ethylene glycol.
4. Heat at 70–80°C for 30 minutes.
5. Filter solution.
6. Titrate with standard benzoic acid solution.
7. Calculate free CaO percentage.

3. Results

Sample	Free CaO (%)
Sample A	0.82
Sample B	2.14
Sample C	1.36

Figure 1 shows the graphical comparison of free CaO content.



3.1 Materials and Samples

Three clinker compositions were studied:

Sample	Composition
Sample A	Limestone + Slag + Clay
Sample B	Limestone + Slag
Sample C	Limestone + Clay + Coal Ash

All samples were burned at 1450°C in laboratory kiln.

3.2 Interpretation

- Sample A showed the lowest free CaO due to better phase formation.
- Sample B showed highest free CaO, likely due to insufficient silica balance.
- Sample C showed moderate free CaO; coal ash contributed reactive silica.

4. Discussion

Sample A exhibited the lowest free CaO content, indicating more complete clinkerization. Sample B showed the highest free lime content, suggesting insufficient silica balance during burning. The presence of coal ash in Sample C improved silica reactivity.

Determination of free CaO helps evaluate lime saturation and kiln performance. Researchers such as Bogue and Taylor contributed significantly to clinker phase chemistry. Studies in Uzbekistan have focused on optimizing raw mixes and using industrial by-products.

The limestone–slag–clay mixture produced optimal clinker mineral formation.

Slag contributed additional silica and alumina, improving lime combination.

The limestone–slag system lacked sufficient alumina balance, leading to incomplete CaO reaction.

The limestone–clay–coal ash mixture showed improved reactivity due to amorphous silica in coal ash.

These findings confirm previous studies that proper raw mix homogeneity reduces free lime.

5. Conclusion

The study confirms that raw mix composition strongly affects free CaO content. The ethylene glycol–benzoic acid method provides reliable results. Limestone–slag–clay composition produced optimal clinker quality.

The investigation confirms that:

1. Free CaO is a critical indicator of clinker quality.
2. Ethylene glycol extraction method provides reliable measurement.
3. Sample A (limestone–slag–clay) exhibited the best performance (0.82% free CaO).
4. Excess free CaO in Sample B (2.14%) indicates incomplete clinkerization.
5. Use of industrial by-products such as slag and coal ash can improve clinker chemistry when properly balanced.

Control of raw mix composition and burning parameters is essential to minimize free CaO and ensure cement durability.

References

1.Bogue, R.H. The Chemistry of Portland Cement.

2.Taylor, H.F.W. Cement Chemistry.

3.Lea, F.M. The Chemistry of Cement and Concrete.

4.Hewlett, P.C. Lea's Chemistry of Cement and Concrete.

5. Tiago Assunçao Santos. Obtenção de clínquer portland a partir da utilização do fino de rocha granítica (frg) e do resíduo de telhas de cimento-amianto (rca) como matérias-primas alternativas. Salvador-2021. 30-35p

6. daxamjonovich, O. Z. A. (2024). ANALYSIS OF THE MAIN TECHNOLOGICAL STAGES IN THE PREPARATION OF CEMENT. Ethiopian International Journal of Multidisciplinary Research, 11(04), 320-324.

7. Orazimbetova, G. J., Adilov, J. K., Nurimbetov, B. C., & Irkahodjaeva, A. P. (2001). Mergel of Karakalpakstan-raw material for producing of portlandcement. UZBEKSKII KHIMICHESKII ZHURNAL, (3), 17-19.

8. Adaxamjonovich, O. Z. A., & Jaksilikovna, O. G. (2024). THE

IMPORTANCE OF CALCIUM OXIDE IN THE PRODUCTION OF PORTLAND CEMENT CLINKER AND THE STEPS OF THE PRODUCTION PROCESSES. Ethiopian International Journal of Multidisciplinary Research, 11(03), 292-295

9. Adaxamjonovich, O. Z. A. (2025, March). COMPREHENSIVE STUDY ON CEMENT: DEFINITION, RAW MATERIALS, AND ADDITIVES. In *Innovative Practices and Research Conference (France)* (Vol. 1, No. 1, pp. 186-189).

10. Grieve, G., & Owens, G. (2004). Sementning 21-asrda taraqqiyotga qo'shgan hissasi.