

**ASSESSMENT OF REBAR CORROSION IN REINFORCED
CONCRETE STRUCTURES USING LASER-INDUCED
BREAKDOWN SPECTROSCOPY**

BY

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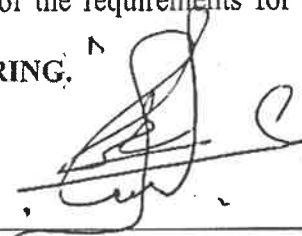


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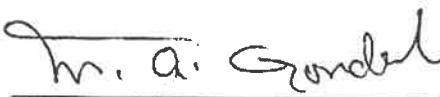
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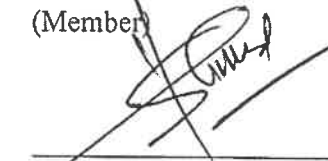
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|Dedicated to my family |

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LIST OF ABBREVIATIONS

LIBS	:	Laser-Induced Breakdown Spectroscopy
SF	:	Silica Fume
FA	:	Fly Ash
EMF	:	Electromotive Force
E	:	Electric Potential
ICCD	:	Image-Intensified Charge-Coupled Device
LoD	:	Limit of Detection
Nd:YAG	:	Neodymium-Doped Yttrium Aluminum Garnet
GGBFS	:	Ground Granulated Blast Furnace Slag
MW-LIBS	:	Microwave-Aided Laser-Induced Breakdown Spectroscopy
XRD	:	X-Ray Diffraction

ABSTRACT

Full Name : AHMED FAISAL SHALABI
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Reinforced concrete structures face significant annual expenditures in combating rebar corrosion, with chloride penetration identified as a major contributor. This study employs Laser-Induced Breakdown Spectroscopy (LIBS) to predict the chloride-induced corrosion rate in such structures quantitatively. Eighty samples, characterized by known chloride content (ranging from 0% to 1.0%), underwent controlled corrosion processes with predetermined degrees measured as bar weight loss. The investigation included two cement types, Type I and Type V, along with samples incorporating pozzolanic materials (FA, SF, and GGBFS) in addition to plain OPC samples. The correlation between rust production rate and chloride concentration was analyzed, and the relationships were established. LIBS was subsequently employed to detect chlorine presence in concrete samples from the same batch, recording the corresponding intensity of the chlorine line. Comparisons with previous studies demonstrated superior conformity of the developed models. The study also presents optimized parameters for the LIBS setup. Notably, results indicated a high correlation between LIBS intensity and chloride concentration, with the developed model accurately predicting the degree of corrosion. |

ملخص الرسالة

الاسم الكامل: أحمد فيصل شلبي

عنوان الرسالة: تقييم تآكل حديد التسليح في المنشآت الخرسانية المسلحة باستخدام التحليل الطيفي للانهييار المستحث بالليزر

التخصص: الهندسة المدنية والبيئية

تاريخ الدرجة العلمية: ديسمبر 2023

النفقات سنوية في مكافحة تآكل حديد التسليح هائلة، وقد تم تحديد الكلوريد كمساهم رئيسي للتآكل. تستخدم هذه الدراسة التحليل الطيفي للانهييار المستحث بالليزر (LIBS) للتعقب بمعدل التآكل الناجم عن الكلوريد في مثل هذه الهياكل كميًا. خضعت ثمانين عينة، تتميز بمحتوى كلوريد معروف (يتراوح من 0% إلى 1.0%)، لعمليات تآكل خاضعة للرقابة بدرجات محددة مسبقًا. شملت الدراسة نوعين من الأسمنت، النوع الأول والنوع الخامس، بالإضافة إلى عينات تحتوي على مواد بوزولانية (FA، SF، وGGBFS) بالإضافة إلى عينات OPC. تم تحليل العلاقة بين معدل إنتاج الصدأ وتركيز الكلوريد وتم تحديد العلاقات. تم استخدام LIBS لاحقًا للكشف عن وجود الكلور في عينات الخرسانة من نفس الخلطة الاسمنتية، وتم تسجيل شدة الإشارة المقابلة لخط الكلور. أظهرت المقارنات مع الدراسات السابقة توافقًا فائقًا للنماذج المطورة. تقدم الدراسة أيضًا معلومات عن طريقة إعداد LIBS للكشف عن الكلورايد. أشارت النتائج إلى وجود ترابط واضح بين إشارة LIBS وتركيز الكلوريد، مع توقع النموذج المطور بدقة لدرجة التآكل.

CHAPTER 1

INTRODUCTION

1.1 General

Concrete, renowned for its exceptional compressive strength, plays a vital role in modern cities, from towering high-rise buildings to various infrastructures. However, its resilience in harsh environmental conditions falls short of its structural might. Notably, the presence of chloride and sulfate ions triggers cracking in reinforced concrete, compromising the strength of its internal rebar [1]. To address this issue, design codes incorporate stringent regulations regarding the permissible levels of chloride and sulfate ions in reinforced concrete [2,3]. Although these regulations enhance the safety and longevity of concrete structures, durability challenges persist. A striking example is the extensive financial losses attributed to corrosion in China, amounting to a staggering 310 billion USD in 2015 [4]. Yet, China is not alone in grappling with corrosion-related concerns. In the United States, corrosion costs escalated from approximately 5.5 billion USD in 1949 to 70 billion USD in 1978, reaching a staggering 276 billion USD by 1998 [5]. Similarly, the corrosion costs in the UK rose from 3.2 billion USD in 1975 to 5.5 billion USD in 1998 [6]. It is not just a matter of cost; rebar corrosion could lead to life-threatening collapses, such as the one showed in Figure 1.

The aforementioned data highlights the imperative need for increased resources and attention towards studying, monitoring, and effectively managing corrosion. To embark on this path, a crucial initial step is gaining a comprehensive understanding of the causes behind rebar corrosion, with the primary culprit being the chlorination of concrete. Chloride is widely recognized as the specific catalyst for steel corrosion in reinforced concrete structures [1,7–10]. In fact, it can be the predominant factor in certain corrosion types, such as pitting corrosion [1]. Consequently, it is unsurprising that numerous studies are solely dedicated to detecting chlorides in concrete. While it is undeniable that chloride represents a major cause of reinforcement corrosion in concrete, it is not the sole contributor to concrete deterioration. Other factors, including cement type, oxygen availability, rebar uniformity, concrete homogeneity, admixtures, carbonation, and sulfate content, all influence the corrosion process. Some factors even exhibit synergistic effects, such as the simultaneous presence of chloride and sulfate ions, prompting their collective examination [11,12]. Unlike concrete chlorination, sulfate attack is not a direct cause of corrosion. However, if corrosion has already commenced due to chloride exposure, the presence of sulfate can intensify and accelerate the corrosion rate. Furthermore, sulfate is known for its detrimental impact on the integrity of concrete, as it reacts with cement components, leading to volumetric expansion. Consequently, this expansion often results in concrete cracking, facilitating the infiltration of various contaminants. In light of these complexities, it becomes evident that a comprehensive approach encompassing the study and management of multiple factors is crucial to effectively combat corrosion in concrete structures.

Various standardized methods exist for quantitatively assessing the extent of corrosion, such as half-cell potential mapping or resistivity mapping [13–15]. While these methods are well-established, they often require significant time and sample preparation. Some of these techniques involve destructive sampling and are primarily suitable for laboratory settings [16]. This is where the laser-induced breakdown spectroscopy method emerges as a valuable alternative. LIBS employs laser pulses to determine the elemental composition of a material of interest [17]. Notably, LIBS is non-destructive, user-friendly, and can be integrated into portable devices. Furthermore, it allows for remote analysis without the need for sample extraction or extensive preparation [18,19]. Consequently, LIBS has found wide-ranging applications across numerous fields. The practical utility of LIBS is evident from the steady growth in annual publications since the early 2000s, with approximately 800 publications in 2019 alone [20]. Many of these studies explore the practical applications of LIBS in areas such as medical, environmental, and engineering fields. LIBS has proven effective in deep-sea exploration, cutaneous element detection, bacteria classification, organic matter detection, soil analysis, and concrete analysis [17,21–27]. Its versatility and adaptability make it a valuable tool for corrosion assessment and monitoring in concrete structures.

The LIBS method involves the conversion of a small amount of the target material into plasma using laser irradiation [28]. The laser generates amplified light through a medium and a series of mirrors that facilitate continuous amplification [28]. Nd: YAG is a commonly used medium for producing lasers in LIBS systems, which induces atomic excitation and transforms the targeted material into plasma. This transformation occurs when the electrons within the material undergo collision and become detached from their

original atoms due to intense heating [17]. Plasma can be characterized by various parameters, one of which is its degree of ionization—the ratio between electrons and other subatomic particles [29]. In the LIBS process, when the laser initially interacts with the target material, it induces high ionization. Over time, the electrons undergo energy level transitions [17,30]. These energy level transitions result in light emission, which is then captured by a spectrometer and analyzed using specialized software on a computer. A typical output from a LIBS analysis is depicted in Figure 2.



Figure 1 The collapse of Genoa Bridge in 2018. Corrosion was one of the major factors of the disaster [32]. Adopted from [33]

LIBS can be used as a handheld device, as shown in Figure 3. However, a more sophisticated setup must be established in a well-controlled environment, such as a

laboratory for testing and verification purposes. A typical LIBS lab setup includes the following components [31]:

- A laser emitter,
- An optical system, which includes two main lenses,
- A spectrometer, and
- A PC to obtain the results.

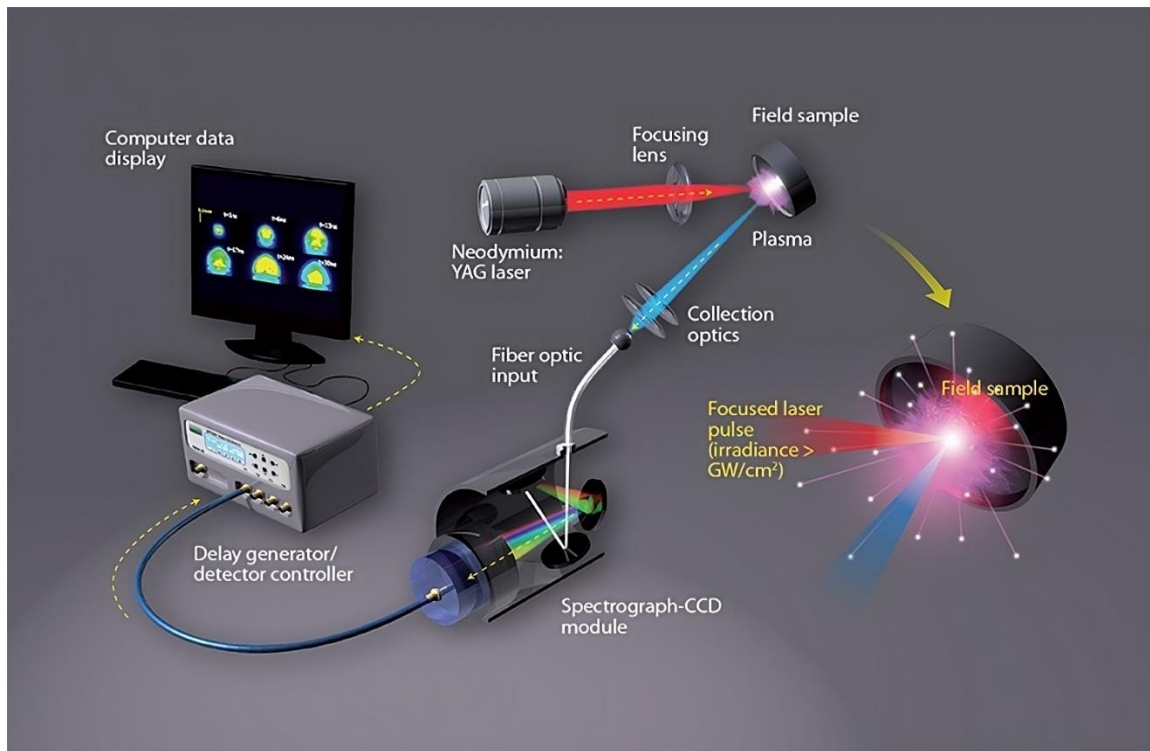


Figure 2 A typical LIBS setup. Adopted from [35].

Figure 4 presents a schematic diagram depicting a typical setup for LIBS analysis. As illustrated, the laser device comprises two mirrors, a laser medium, and a pump light source. In most cases, Nd: YAG serves as the preferred laser medium for LIBS applications [23,26,31]. However, other laser mediums are also employed, each with unique

advantages. Examples include the Excimer laser, which utilizes a gaseous medium, and the carbon dioxide laser. Nevertheless, Nd: YAG stands out due to its compact size, making it particularly suitable for portable instruments [17,18]. It is worth noting that the specifications of portable and laboratory Nd: YAG lasers differ. The handheld version, for instance, is approximately 70 kg lighter than its laboratory counterpart [17]. This weight difference stems from the design considerations of laboratory instruments, which prioritize high accuracy, maximum stability, and energy output to cater to a wide range of applications.



Figure 3 Handheld LIBS devices. Adopted form [24].

A typical LIBS setup incorporates two main lenses or optical systems, as depicted in Figure 4 and a typical output of LIBS is shown in Figure 5. One lens is responsible for focusing the laser beam, while the other collects the emitted light. A focusing system is employed to generate plasma using LIBS. Comprising lenses or mirrors that concentrate the laser beam onto a smaller spot [29,32]. The simplest form of this system involves a single

focusing lens, suitable for situations where the sample-to-lens distance remains fixed. A combination of mirrors and lenses is utilized in applications requiring adjustable focus or lens-to-sample distance, such as certain industrial settings [32–34]. Moreover, the laser beam can be expanded to cover a larger sample area using a cylindrical lens, resulting in a longer spark and enabling quick scanning of larger samples [17]. The primary function of the second lens or optical system in LIBS is to collect the emitted light. While a single lens setup is straightforward, a multi-lens arrangement may be employed in specific cases [17,21].

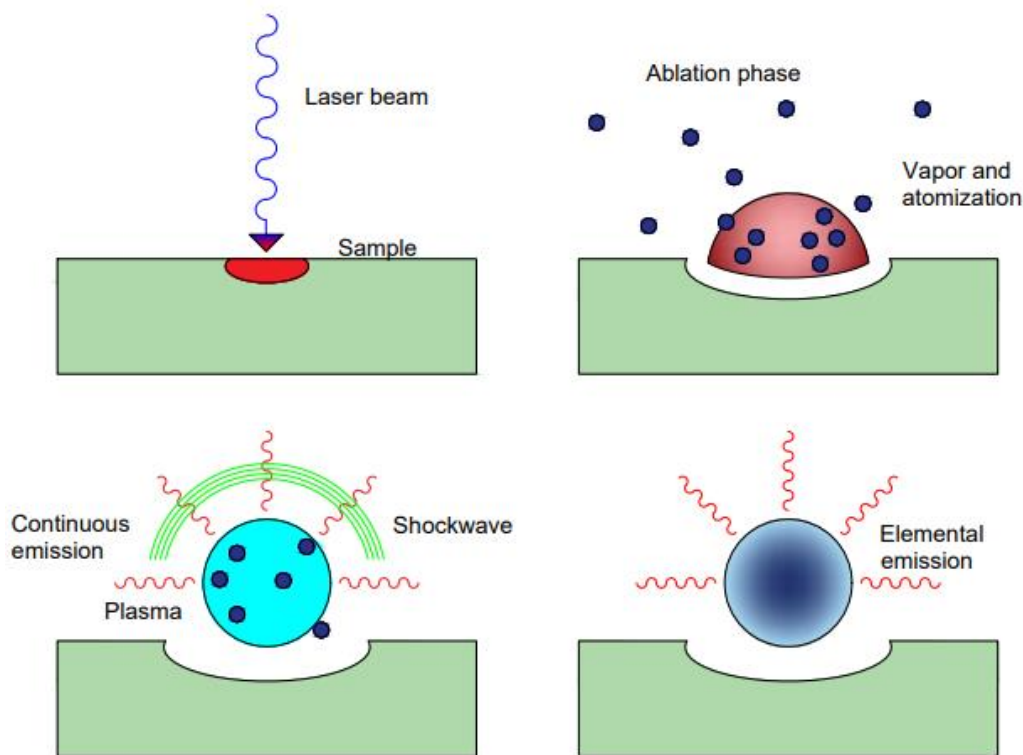


Figure 4 The working principle of LIBS. First the laser hits the sample, causing a material ablation, vaporization, and atomization. Continuous emissions are then generated and elemental emissions as well

In recent times, there has been a notable surge in research focusing on the utilization of LIBS for concrete analysis [33–39]. Specifically, LIBS has shown promise in the detection of rebar corrosion [40–44]. This research area is particularly active due to the non-

destructive nature and user-friendly characteristics of the LIBS technique. Recent studies have also indicated that LIBS holds significant potential as a reliable and accurate method for detecting contaminants in concrete [44–46]. Notably, research utilizing LIBS for chloride content detection in concrete [44,46,47] has demonstrated its ability to detect chloride concentrations up to the maximum allowable limits in prestressed concrete structures, such as 0.2% by mass of cement [2]. Similarly, the versatility and portable nature of LIBS-based devices, coupled with minimal sample preparation requirements, have the potential to revolutionize concrete testing methods.

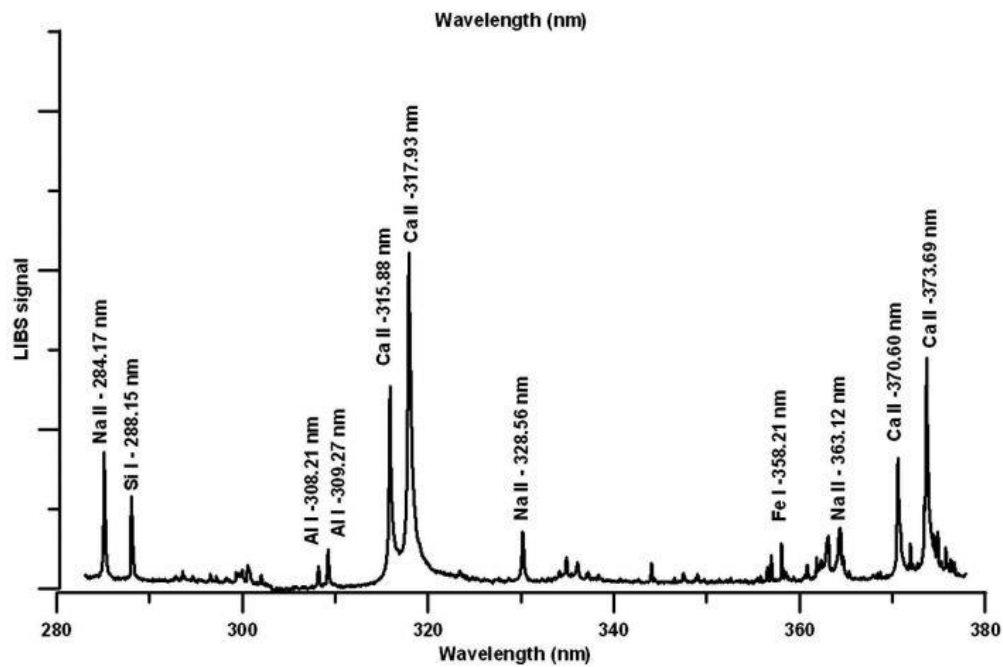


Figure 5 Typical LIBS output. Adopted from [17].

However, while interpreting LIBS output or operating the device, it is important to consider certain limitations and precautions, such as the matrix effect, sample homogeneity, and lens-to-sample distance [17,28], which can impact the reliability and limit of detection (LOD) of the technique. To mitigate the influence of sample-dependent properties, calibration techniques have been established. These methods include calibration curves and

calibration-free LIBS [48–53], each with its own advantages and applications. Furthermore, additional practices and techniques have been adopted to enhance the accuracy of LIBS analysis. Examples include the utilization of dual-pulsed laser systems and adjustable optical systems. Overall, the increasing adoption of LIBS in concrete analysis, along with ongoing efforts to address limitations and refine calibration techniques, has the potential to significantly advance the accuracy and reliability of concrete testing methods.

In summary, rebar corrosion in reinforced concrete is a significant and costly issue influenced by various factors, including chloride penetration and sulfate attack. Despite the implementation of design codes and regulations to mitigate corrosion effects by restricting chloride and sulfate content, many reinforced concrete structures still face the challenges of chlorination and sulfate attacks. Ongoing efforts continue to study, analyze, and monitor these phenomena, with laser-induced breakdown spectroscopy (LIBS) emerging as a recent technological advancement for these purposes. LIBS employs laser technology to analyze the elemental composition of a target material.

1.2 The objectives

By the end of this research, the following tasks are expected to be accomplished:

- 1- To assess the ability of LIBS to detect chloride in concrete samples without sample preparation (testing concrete as it is).
- 2- To develop a correlation between the output of LIBS (intensity) and the corrosion degree.

CHAPTER 2

LITERATURE REVIEW

Corrosion refers to the conversion of iron into iron oxide as a consequence of harsh environmental conditions [1,54]. This transformation is undesirable as iron oxides lack the favorable properties of iron. Consequently, any conversion from iron to iron ions represents a loss. Such loss directly diminishes the load-carrying capacity of concrete members since it is equivalent to reducing the diameter of the rebar. Extensive investigations [55,56] have revealed that even a modest 9% reduction in rebar diameter can lead to a noticeable decrease in yield and ultimate strengths. Furthermore, the diminished cross-section of the rebar has adverse effects on its fatigue strength [55–60] and weakens the bond between concrete and steel [61–63]. However, the reduction in rebar cross-section is not the sole consequence of corrosion. Corrosion also induces cracking in concrete because the volume of rust products is significantly greater than that of iron in its original state [58,64–66], as illustrated in Figure 6. The formation of cracks in concrete, in turn, intensifies the corrosion rate since cracks serve as pathways for contaminants, air, and water to penetrate the concrete and reach the surface of the rebar. Additionally, corrosion gives rise to several ancillary effects. One such effect is hydrogen embrittlement of the rebar [67,68], wherein the diffusion of hydrogen ions causes the metal to lose its ductility and become brittle. This loss of ductility is highly undesirable as it can potentially lead to catastrophic failure of the concrete member. The consequences of corrosion encompass not only the reduction in rebar cross-section and the initiation of cracks in concrete but also the associated

weakening of bond strength and the detrimental effects of hydrogen embrittlement. Addressing and mitigating corrosion-related challenges is vital to ensure the long-term structural integrity and durability of concrete components.

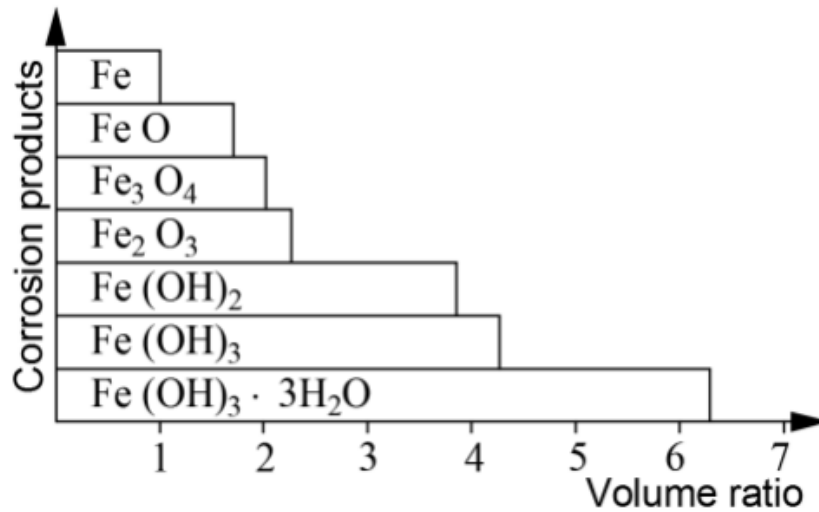


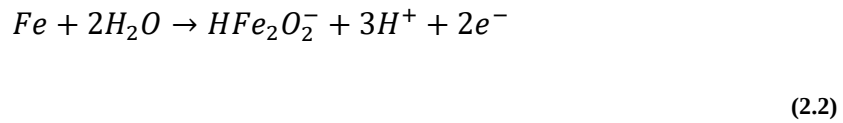
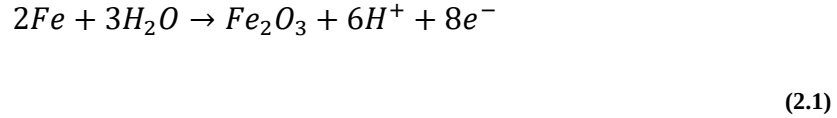
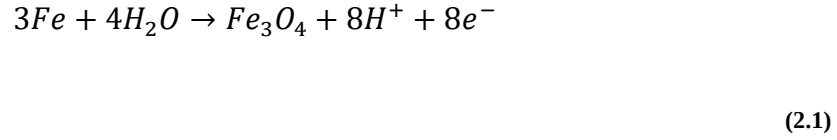
Figure 6 The volume of iron compared to the other rust products. Adopted from [28].

With a stronger emphasis on the use of LIBS to assess the corrosion condition in reinforced concrete buildings, this MS thesis focuses on the latest advancements and difficulties in the application of LIBS for corrosion engineering. Additionally included in the study are the frequently used calibration-free LIBS techniques, like the usage of AI. A brief overview of LIBS's history and a discussion of how LIBS is applied in various disciplines have also been provided. There are still certain obstacles to overcome despite how reliable LIBS research is. Chemical applications such as the identification of contaminants typically rely on the detection of certain elements or ions. The use of a correlation between the chemical components and the required parameters, however, may be necessary for physical and mechanical applications such as material heterogeneity and, in certain situations, humification degree. Therefore, this thesis covers the advantages of using LIBS to accurately identify the corrosion state and discuss the potential applications of this technology in corrosion engineering.

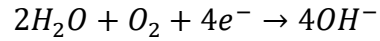
2.1 Corrosion of reinforced concrete structures

For corrosion to occur, certain conditions must be present. Even in the presence of chloride and sulfate ions, corrosion may not transpire if these conditions are not met. Concrete itself acts as a natural protector for rebar due to its high pH level, typically ranging from 13 to 13.8 [1,69,70]. Steel develops a protective layer known as the passive film within this highly alkaline environment. However, this film is only a few nanometers thick and can be compromised by carbonation or chlorination of the concrete, a process referred to as de-passivation [1,71–73]. Once de-passivation occurs, several factors come into play to determine the corrosion rate, such as the intensity of the current flowing within the corrosion cell. A corrosion cell consists of an anode, a cathode, an electrical connection (conductor), and an electrolyte [1]. The anode serves as the terminal from which electrons leave the system, while the cathode is the terminal to which electrons migrate. Electrical conductivity is crucial as it enables the transfer of electrons from the anode to the cathode. The electrolyte is also vital as a medium for ion transfer. Accumulation of ions on one side of the cell impedes corrosion, as the formation of iron ions, which is essentially the corrosion process, cannot occur under such conditions [1,74], as illustrated in Figure 7. In reinforced concrete, the rebar acts as a mixed electrode where both the cathodic and anodic reactions take place, while the concrete acts as the electrolyte for ion transfer. This arrangement is known as a microcell. In contrast, a macrocell involves the occurrence of anodic and cathodic reactions in separate areas of the rebar [1,75]. The chemical reactions within a corrosion cell can be categorized into two main reactions: anodic and cathodic reactions. The anodic reactions involve the formation of rust products, representing the side where rust develops. Conversely, on the cathodic side of the cell, the primary product is

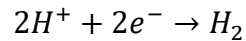
alkalinity, a property of concrete that protects the steel. The four main reactions occurring on the anodic side are as follows [75]:



The first two reactions are passive in nature and cause no corrosion damage and they can occur in high-quality concrete where the pH is around 13.5. The third reaction involves forming iron oxyhydroxide, a form of rust that can cause cracks in concrete structures due to its relatively large volume. The last reaction involves a direct dissolution of iron and occurs when the pH of concrete drops significantly [1,75–77]. On the other side of the cell (i.e., the cathode), the following two different reactions occur [75]:



(2.4)



(2.5)

Equation (5) explains why the cathodic part of the rebar does not corrode; instead, it gains more resistance to corrosion due to the formation of hydroxyl ions. Unlike the fifth reaction, the sixth one has a negative effect. It causes hydrogen embrittlement due to the formation of hydrogen ions [67,68]. While corrosion can't occur in reinforced concrete structures without a complete corrosion cell, the corrosion process may involve more than just the basic half-cell reactions described earlier. Chloride and sulfate ions, for instance, play a major role in the corrosion of reinforced concrete.

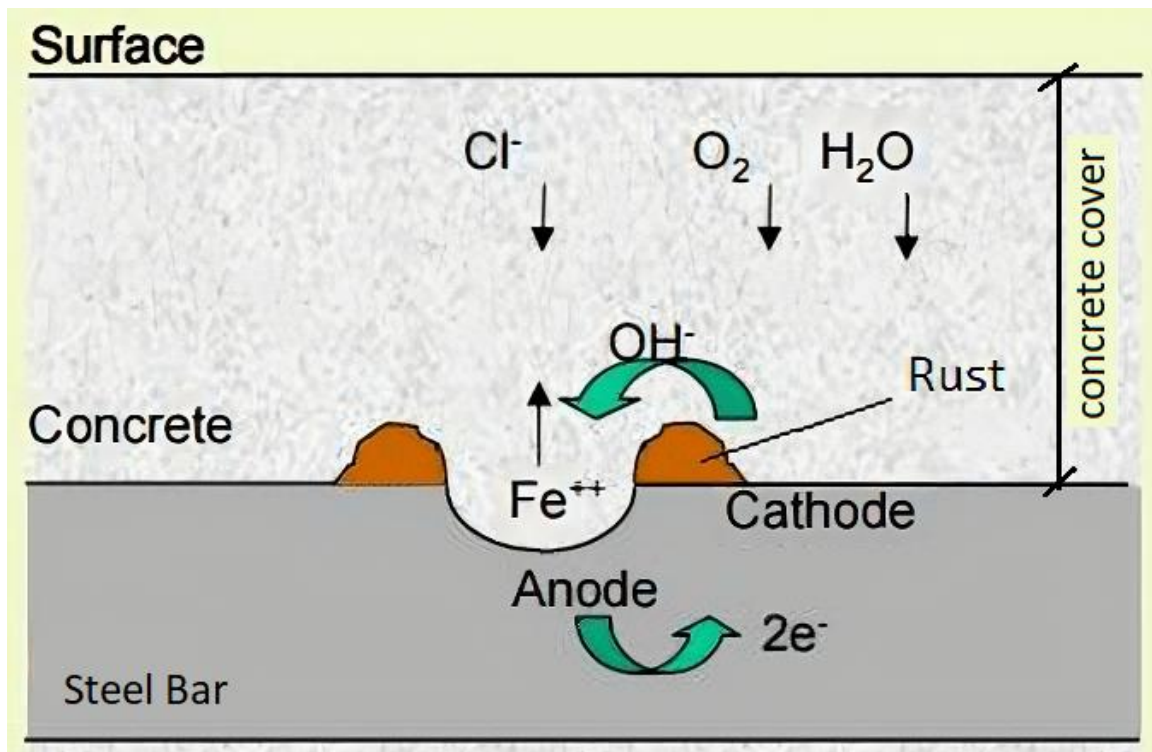


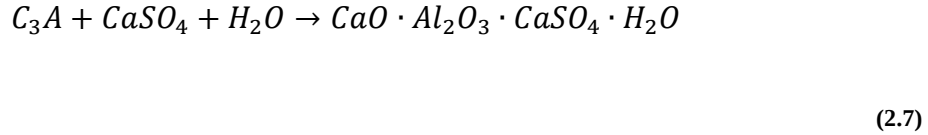
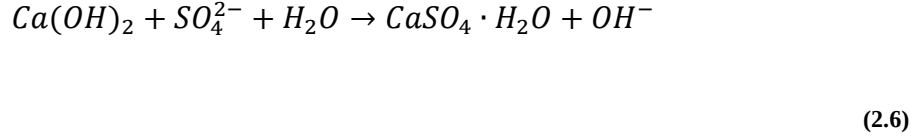
Figure 7 A typical corrosion cell. Adopted from [72].

Two main types of corrosion are commonly observed: uniform corrosion and pitting corrosion. Uniform corrosion occurs when rust develops uniformly around the rebar and is often associated with concrete carbonation. Conversely, pitting corrosion involves the formation of rust in scattered spots on the rebar, typically linked to chloride attack [1,78–81]. Chloride is recognized as the primary and specific corrosive agent in reinforced concrete, leading to the establishment of strict regulations within design codes regarding durability requirements for chloride exposure and the allowable chloride content in concrete mixes. This is because chloride targets the vulnerable areas of the rebar's passive film, resulting in localized corrosion, which is more concerning than uniform corrosion due to its challenging detection [58,82–84]. Chloride can originate from both internal and external sources. Internal factors include contaminated concrete components such as sea-dredged aggregates, saline mixing water, and chloride-based admixtures (although the usage of such admixtures in reinforced concrete has significantly diminished over time) [1]. Calcium chloride, a previously employed accelerator, is an example of a chloride-based admixture. In the past, chloride dosages from such accelerators could exceed 2% by mass of cement [85,86], a significantly high amount by modern standards [2]. As illustrated in Figure 7, the rate of the cathodic reaction is influenced by the availability of oxygen [87]. Consequently, the chloride threshold value depends on the oxygen availability, which in turn is dictated by the exposure conditions. In the worst-case scenario of structures exposed to air, the chloride threshold value ranges from 0.4% to 1% by mass of cement [1]. For prestressed concrete structures, the allowable chloride concentration can be as low as 0.2% by mass of cement [2]. Other factors also impact the permissible chloride content in reinforced concrete besides exposure conditions. The free/total chloride ratio is commonly

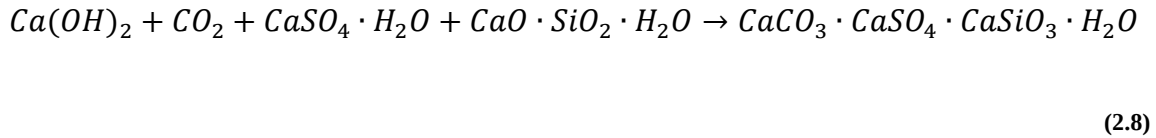
used to describe the allowable chloride content for corrosion prevention [88]. Chloride in concrete exists in both free and bound forms, with the sum of free and bound chlorides referred to as the total chloride content. It was previously believed that bound chloride played no role in the corrosion process, and corrosion in reinforced concrete only occurred due to free chloride. While it is true that free chloride contributes to corrosion, recent research suggests that bound chloride can be released and further accelerate corrosion if the pH level drops [89–91]. This highlights the usefulness of expressing the chloride content as a ratio between Cl^- ions and OH^- ions, reflecting the pH level and providing valuable insights into corrosion risk.

Sulfate ions represent another significant factor driving corrosion. It is widely recognized that sulfate can cause volumetric expansion of concrete [92,93]. This expansion introduces tensile stresses in restrained concrete members, which is highly undesirable considering that concrete possesses relatively low tensile strength compared to its compressive strength. The presence of cracks in concrete indirectly influences the corrosion rate as it provides pathways for the ingress of surrounding contaminants. However, a lesser-known aspect of sulfate is its potential impact on the corrosion rate [11,12,94–97]. This effect can be either positive or negative, contingent upon the exposure duration and the specific concrete mix design [94,98]. Nevertheless, it is generally advisable to minimize concrete exposure to sulfate ions. Sulfate contamination commonly originates from sources such as polluted soil, which, when combined with rainwater, can further contaminate groundwater, making it a potential source of sulfate as well [70]. Other sources of sulfate include seawater, chemical waste, and fertilizers [99]. Upon reaching the concrete, sulfate reacts

with calcium hydroxide (Ca(OH)₂) to form gypsum or reacts with calcium aluminate (C₃A) to produce ettringite, as illustrated below [75]:

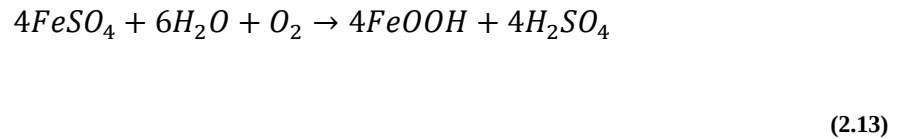
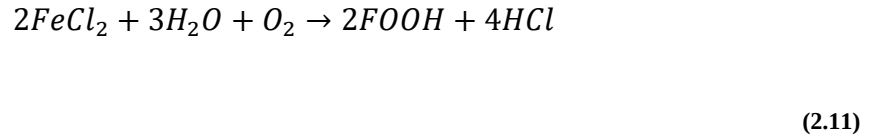
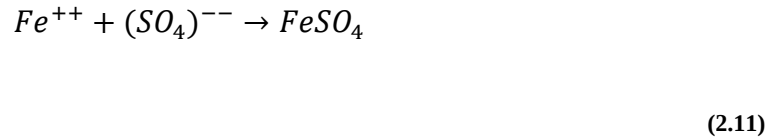
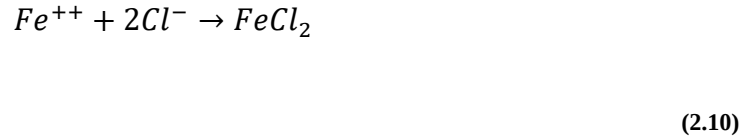


The formation of ettringite is the most concerning reaction, particularly when high C₃A cement is used. It causes much more volumetric expansion of concrete, producing tensile stresses that the concrete cannot withstand. Hence, the ettringite also weakens the paste-aggregate bond because it usually accumulates on the aggregate surface [92]. Under very special conditions, namely a carbonated concrete in a cold and very humid exposure (R.H. > 95%), sulfate can result in a complete loss of concrete strength due to the following reaction [1]:



The combined action of chloride and sulfate affects the rate of corrosion as well [11,12,95,96,100]. Some researchers suggest that sulfate can reduce the chloride binding and, thus, increase the severity of chloride attack [98]. Some others, however, suggest that sulfate can decrease the rate of chlorination by filling the pores in concrete with the sulfate reaction products [101]. This claim is supported by other studies [94]. The studies show contradictory results because a different exposure time and mix design have been used in each study. The effect of sulfate on rebar corrosion was addressed by Al-Amoudi, where

rebar steel was embedded in cement paste and exposed to sulfate, chloride, and sulfate-chloride solutions [12]. The results indicate that sulfate alone has minimal effect on rebar corrosion unless it is mixed with chloride. In such cases, the increase of sulfate concentration in a given chloride concentration was found to increase the corrosion rate up to two times, depending on the sulfate concentration. The following reactions explain how sulfate accelerates the corrosion rate [12,102]:



The corrosion process in reinforced concrete involves several consecutive reactions. The initial reaction (Equation 10) is the dissolution of iron into the concrete, resulting in the formation of ferrous ions and electrons. This is followed by the subsequent reactions (Equations 11 and 12), where ferrous ions react with chloride and sulfate ions to form ferrous chloride and ferrous sulfate, respectively. The fourth and fifth reactions occur in the presence of oxygen and moisture (Equations 13 and 14). In the fourth reaction, ferrous

chloride is converted into iron oxyhydroxide and hydrochloric acid, while in the final reaction, ferrous sulfate is converted into iron oxyhydroxide and sulfuric acid. The acids generated from these reactions further react with the rebar, leading to the formation of more ferrous chloride and ferrous sulfate. Design codes typically express the allowable concentration of sulfate in concrete in terms of water-soluble sulfate [2]. According to [2], sulfate concentrations below 150 ppm are generally not a cause for concern, and no specific regulations regarding the water-to-cement ratio (w/c) or cement type are imposed in such cases. However, when the sulfate concentration exceeds 150 ppm, the potential for sulfate attack becomes a concern, and the maximum allowable w/c ratio decreases as the sulfate concentration increases. Additionally, the severity of sulfate attack is influenced by the content of calcium aluminate (C3A), with higher C3A contents exacerbating the potential for sulfate attack [92]. Therefore, it is recommended to limit the C3A content to 3 to 5% in sulfate-resistant concrete (typically achieved by using Type V cement) [92]. By controlling these factors, the risk of sulfate attack can be effectively managed in concrete structures.

2.2 Advantages of LIBS over conventional corrosion-assessment techniques

While the recovery of corroded rebar is not feasible, assessing corrosion is crucial to prevent further complications. The assessment process typically commences with a visual inspection of areas that are prone to corrosion or where corrosion damage has already occurred. Signs of corrosion encompass hairline cracks, rust stains, and concrete spalling. However, the detection of corrosion is not always as straightforward as visually identifying a rusty spot on a slab or beam. Pitting corrosion, for instance, can occur and propagate without displaying any visible indications [82]. Unfortunately, pitting corrosion is the most

prevalent form of corrosion in reinforced concrete (RC) structures and accounts for approximately 70% of corrosion cases [103]. Moreover, it is important to note that cracks in RC structures can stem from various causes. Therefore, it would be inaccurate to generalize that any crack in a concrete member is solely attributable to corrosion, as depicted in Figure 8 and Table 2. Consequently, more sophisticated methods have been developed to detect and assess corrosion accurately.

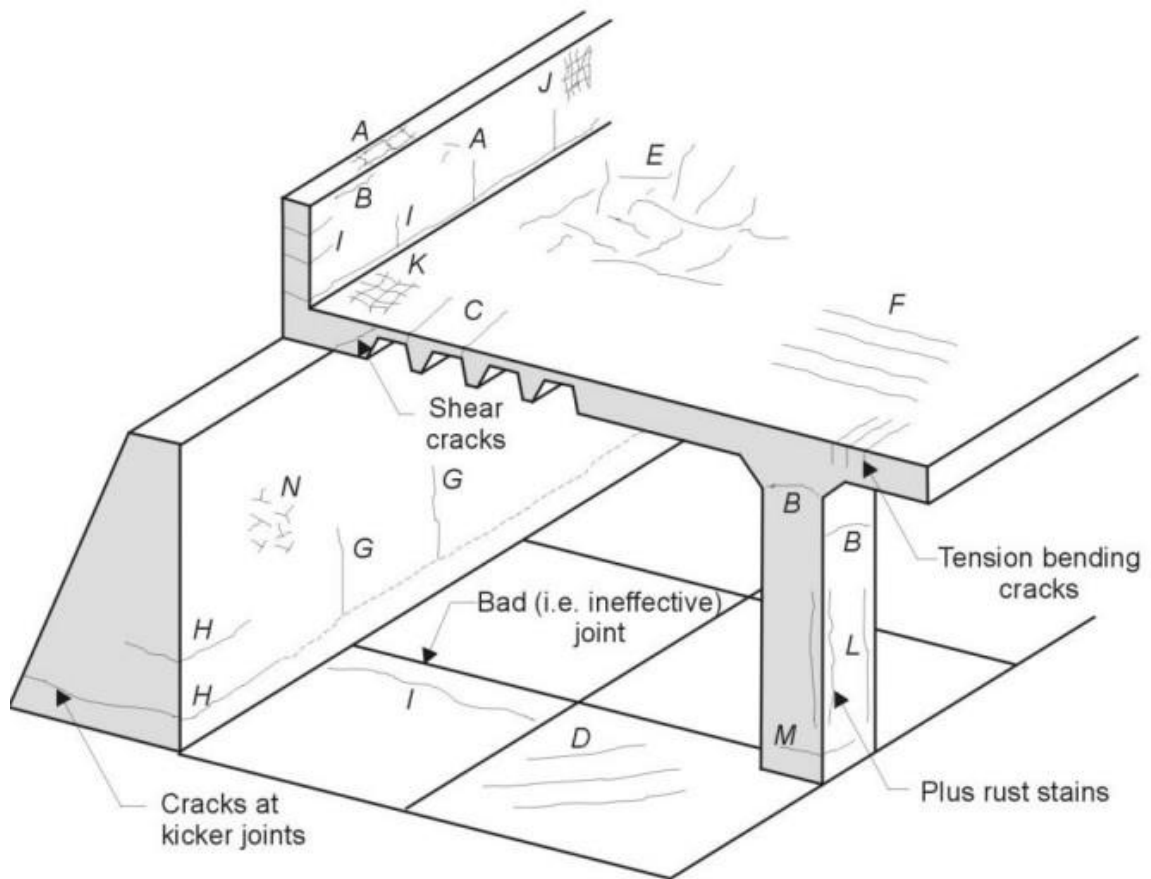


Figure 8 Types of cracks in reinforced concrete structures; adopted from [1]. The causes of these cracks are explained in Table 1.

One of the old methods used in corrosion monitoring is the half-cell potential measurement, also known as half-cell potential mapping. In this method, the potential of the corrosion cell is measured between a reference electrode and the embedded steel bar in the concrete using a voltmeter with an electrical connection between the reinforcement bar and the

voltmeter. Also, a conductive solution should be applied at the end of the reference electrode, as per the ASTM standard [14]. This technique can be used for the following purposes [104]:

- Locating corroding rebar,
- Defining the locations at which more comprehensive analysis should be conducted,
- Evaluating the state of corrosion after repair work and
- Defining the layout of protection systems.

Table 1 causes of cracks in reinforced concrete structures.

Type of cracking	Subdivision		Most common location	Primary cause (excluding restraint)	Secondary cause/factors	Time of appearance
Plastic settlement	A	Over reinforcement	Deep sections	Excess bleeding	Rapid early drying conditions	10 min to 3 h
	B	Arching	Top of columns			
	C	Change of depth	Waffle slabs			
Plastic shrinkage	D	Diagonal	Road and slabs	Rapid early drying	Low rate of bleeding	30 min to 6 h
	E	Random	R.C. slabs			
	F	Over reinforcement	R.C. slabs	Rapid early drying, steel near surface		

Early thermal contraction	G	External restraint	Thick walls	Excess heat generation	Rapid cooling	1 day to 2 – 3 weeks
	H	Internal restrain	Thick slabs	Excess temperature gradient		
Long-term drying shrinkage	I		Thin slabs (and walls)	Inefficient joints	Excess shrinkage, inefficient curing	Several weeks or months
Crazing	J	Against formwork	fair-faced' concrete	Impermeabl e formwork	Rich mixes Poor curing	1 – 7 days sometimes much later
	K	Floated concrete	Slabs	Over-trowelling		
Corrosion of reinforcement	L	Natural	Column s and beams	Lack of cover	Poor-quality concrete	More than 2 y
	M	Calcium chloride	Precast concrete	Excess calcium chloride		
Alkali-aggregate reaction	N		Damp location s	Reactive aggregate plus high-alkali content		More than 5 y

The technique has been in use since 1977, receiving initial approval and subsequent reapprovals in 1999 (ASTM C876-91) and 2009 [14]. Despite its long history, this method still possesses certain critical limitations. Specifically, it is sensitive to changes in concrete resistivity and the presence of stray currents within the concrete. This introduces complexities, as stray currents themselves can contribute to rebar corrosion [14,69]. Another source of error in this method is the moisture content of the concrete. In the half-

cell potential measurement method, which involves measuring the potential of a corrosion cell, the voltage measurement is influenced by the resistivity of the concrete. Therefore, any variations in the resistivity of the concrete can lead to unreliable readings. Moisture content changes are one factor that can impact concrete resistivity [104]. Furthermore, determining the corrosion state based solely on this test is not straightforward. While the ASTM standard establishes certain fixed potential values corresponding to the possibility of corrosion, it has been shown in some tests that the measured potential alone is insufficient to indicate the likelihood of rebar corrosion [14,105]. Moisture, temperature, concrete cover thickness, chlorination, and carbonation of concrete, as outlined in [1], all influence the potential value that may lead to corrosion. Although [105] provides some guidelines for interpreting half-cell potential measurements, the numerous influencing factors involved can reduce the accuracy of this method.

Another indirect method for assessing the corrosion state in reinforced concrete (RC) structures is resistivity mapping. The electrical resistivity of concrete serves as an indicator of its corrosion resistance; higher resistivity implies greater corrosion resistance, while lower resistivity suggests a higher susceptibility to corrosion. This is because the corrosion process involves the migration of ions through the concrete, which is hindered by the electrical resistance of the material. Also, resistivity measurements can help identify the most porous concrete areas where contaminants can penetrate more easily [1]. In resistivity mapping, a direct or alternating current is applied to the concrete through two outer electrodes, and the resulting potential between two inner electrodes is recorded. This method offers several advantages [106]:

- Fast measurement,
- Indicates concrete durability,
- Identifies defect points and
- Indicates corrosion rate qualitatively.

However, no direct correlation between concrete resistivity and corrosion rate has been established. In addition, the concrete resistivity varies from 100 to 100,000 $\Omega \cdot m$. It is influenced by temperature, relative humidity, rebar orientation, and w/c ratio [106], which may introduce inaccuracies in the determination of corrosion rate.

Various chemical methods are employed to assess the presence of contaminants, such as chloride, and evaluate the corrosion state. Multiple techniques exist for determining the chloride content in concrete. One widely recognized method involves spraying a sliced concrete sample with silver nitrate, which produces a distinct silver coloration in the chlorinated regions [107,108]. Combining chloride profiling with half-cell potential mapping can help establish the chloride threshold for a given structure. Additionally, empirical relationships between chloride concentration and half-cell potential can be established for specific structures. However, chloride testing methods are often categorized as either rapid but less accurate or accurate but time-consuming. Rapid methods are typically utilized in the field, while more accurate tests are conducted in laboratories. It is important to note that many chloride detection methods require sample preparation [1].

The adoption of laser-induced breakdown spectroscopy (LIBS) as an analysis method is increasingly prevalent in various industries [32–35,38,109]. This trend highlights the

advantages and utility offered by this technique. Several recent studies have integrated LIBS with chemometrics-based techniques to investigate different physical properties such as soil unconfined compressive strength and moisture content [110,111]. Noteworthy advantages of utilizing LIBS over conventional analysis methods include the following [32–34]:

1. Remote analysis: LIBS analysis instruments can be seamlessly integrated into portable devices [112], enabling easy deployment in the field. No other concrete analysis method provides such a convenient and field-ready approach. Moreover, laser beams possess the capability to travel over long distances, theoretically allowing concrete analysis from remote locations.

With the appropriate setup, the analysis can be conducted at tens of meters. This has been demonstrated in [113] where a high-energy, ultrashort filaments generated laser pulses has been used to conduct LIBS analysis at 90 m. The technique used in that letter is based on filament-induced LIBS (R-FIBS or FIBS), which is yet another analytical method that can be used to enhance some spectroscopic features of LIBS [114]. Conducting such a long-distance analysis in the aforementioned study was possible due to the filaments (propagation of laser without diffraction) arise when the ultrashort pulses and balanced focusing/defocusing cycles. Due to this phenomenon, a laser intensity of 10^{13} W/cm² can be carried over several kilometers [113,115], which is enough to ablate metals [113]. The mentioned study claims that R-FIBS can be applied up to the kilometer range, but their experiment was limited by the available space in front of the laser setup [113]. The laser used in that setup was a 250 mJ called Teramobile at 10 Hz centered at 800 nm with 30 filaments along the beam and two

samples were considered: a copper plate and a steel plate. One downside to this high-intensity laser is that it left over a damage over a few square centimeters on the sample surface [113].

Although the previous research was focused on analyzing metals, but long-distance LIBS is not limited to metals only. For example, in [116], LIBS was used to analyze rocks at a 7 m distance; a significantly shorter distance than the previous study due to the different purpose of the experiment. Such a distance is still considerably longer than a typical lab setup, nonetheless. A 10 Hz, 1064 nm Nd:YAG laser with pulse energy of 17 mJ/pulse was used and the samples were placed in a ~7 Torr CO₂ chambers at 7 m away to simulate the MSL ChemCam setup. To take into the account the sample heterogeneity, the samples were pressed into pellets and the spectra was collected from at least 5 spots from each sample. The study discussed the usage of 3 multivariate methods (partial least square, multilayer perception artificial neural networks, and cascade correlation) to optimize LIBS results in the given environment. The results implicitly show that an elemental analysis at this distance is defiantly possible and can be further enhanced with the appropriate data analysis method especially if the training sets for AI methods were grouped carefully, which can be achieved by categorizing the samples according to their spectra using partial least square, for example [36,117–122].

Remote minerals detection at 15 m was also accomplished in [123] where a 1064 nm, Q-switched Nd:YAG laser that has 10 ns pulse width, 10 Hz, and 400 mJ max pulse energy combined with a single lens-based signal collecting subsystem that covers the 200 to 750 nm range was used. A custom optical component that combines six times beam expander with a telescope was used to focus the laser as well. The goal of the

study was to test the setup's ability to detect an ore at the specified distance with the help of a proposed multi-spectral line calibration method. To validate the results, chemical analysis was done to spot the elements of interest in the ore, which in this case was Cu. The results from a single-wavelength method were also obtained and compared with the proposed method to assess the usefulness of the latter one. When using the mentioned setup with the proposed method, the Cu content of the ore was found to be 1.24%, which agrees with the result of the chemical analysis, that is 1.244% and hence confirms the ability of LIBS to perform distant analysis.

LIBS can also be integrated in portable devices. However, such devices are less capable than laboratory setups [17,18,112,124]. For example, the pulse energy of a dedicated laboratory setup can reach up to 450 mJ while it does not usually exceed 25 mJ in compact devices [17]. There are some exceptions where compact devices can supply a 150 mJ laser, such as the CNR Applied Laser Spectroscopy Laboratory and Marwan Technology devices "MODI", but such devices usually sacrifice portability for power [125]. In MODI's case, the device is comprised of cabinet on wheels to contain the LIBS setup and a PC, while mobile, it is certainly not as portable as handheld devices. Other attributes of portable and lab lasers differ as well, such as the pulse width, energy stability of cooling solution. Table 2 compares the specifications of typical compact and laboratory Nd:YAG setups.

The reviewed literature confirms that LIBS can be used remotely, but special equipment might be required. Such as powerful focusing lenses or high pulse energy, which might not be available in handheld devices. However, portable devices can be incorporated into drone or other forms of mobile devices to conduct remote analysis by

different means. Overall, the literature showed that it is possible to conduct remote LIBS analysis.

2. Multi-element detection: Traditional concrete testing methods often focus on detecting a single element, such as chloride or sulfate. Each test necessitates its own specific procedure, equipment, calibration method, and interpretation technique. In contrast, LIBS analysis is universally applicable to all elements. For instance, the same setup employed for detecting chloride can be used to detect sulfate, oxygen, or any other element. This significantly reduces the cost and complexity associated with concrete testing.
3. Real-time analysis: LIBS analysis offers faster results compared to typical concrete testing methods. The time-consuming sample preparation and testing procedures required in conventional methods are circumvented with LIBS analysis. The absence of specialized sample preparation streamlines the testing process, saving time and effort.
4. Virtually non-destructive testing: Conventional concrete testing requires obtaining a sample of the concrete body, commonly through concrete coring. This process involves removing concrete cylinders from the structural element to be analyzed. Core samples are necessary for comprehensive mechanical tests and even for chemical tests such as chloride profiling, for example. Unfortunately, the usage of LIBS does not completely eliminate this necessity, yet it can be utilized to minimize destructive tests in cases of preliminary surveys for rust detection, for example. Rust stains are sometimes formed on the surface of the concrete member due to corrosion attack. These stains on the surface can be analyzed using LIBS to confirm corrosion of rebar [126], which is useful

because reddish stains are not always due to rebar corrosion. For example, sulphate inclusions or pyrrhotite reaction with mortar can result in brownish stains and be mistaken for rust stains [127–129]. Coring is not feasible for critical members as it can compromise their capacity. This process necessitates specialized equipment, and the obtained cylinder must meet specific specifications for diagnostic purposes. In such application, only a few milligrams of the targeted member are ablated by the laser, which is not usually an issue in case of concrete analysis.

5. Quantitative results: Some concrete testing methods offer qualitative criteria to describe rebar corrosion, while others provide only rough quantitative results. In contrast, LIBS analysis consistently provides precise quantitative measurements of contaminant concentrations.

2.3 Interpretation of LIBS results and error sources

The emission spectrum captured from a single plasma is the fundamental element of every LIBS experiment, whether qualitative or quantitative analysis is used [34,130,131]. A portion of the sample within the laser plume area is atomized with each laser pulse, creating a plasma that excites and re-excites the atoms to create light, and, thereafter, many techniques have been developed to overcome such limitations [22,68,132–134]. A measurement is produced once the plasma light is gathered and recorded. The measured quantities might be the emission wavelength of a single line or group of lines, or a spectral area (for example, as determined by an image-intensified charge-coupled device (ICCD) detector). The intensities of the analyte emission lines are calculated from the spectra [38,51,135].

2.3.1 The matrix effect

The typical output of laser-induced breakdown spectroscopy (LIBS) is generally represented as a graph illustrating intensity versus wavelength, similar to the example shown in Figure 5. Each element exhibits a characteristic range of wavelengths that are utilized for its detection. However, it is important to note that the wavelength of an element can vary between different samples [17,32]. This phenomenon is known as the matrix effect, wherein the physical or chemical properties of the sample, such as the concentration of certain elements, can influence the signal emitted by other elements. For instance, if the presence of silicon needs to be determined in both a soil sample and a steel alloy using LIBS, the signal emitted by silicon in the soil sample would differ from that of silicon in the steel alloy, even if the silicon concentration is the same in both samples. The presence of water also impacts the signal strength [35], posing challenges in applications like underwater exploration, environmental monitoring, or fresh concrete analysis. Furthermore, the matrix effect is noticeable even in samples with similar chemical compositions, such as soils and stream sediments [37]. This problem is also very apparent in concrete analysis due to the excessive amount of calcium in cement [43]. Understanding and accounting for the matrix effect is crucial for accurate and reliable interpretation of LIBS results in various sample types and environments.

The signal emitted from an element in laser-induced breakdown spectroscopy can also be affected by differences in the physical properties of a sample, such as its specific heat and thermal conductivity. This phenomenon, known as the physical matrix effect, represents a subdivision of the overall matrix effect [37]. Granular materials, such as aggregate or cement clinker and powder, can exhibit a more pronounced physical matrix effect during

analysis [37,39,136–138]. In these cases, larger particles within the soil matrix may not completely evaporate, thereby preventing access to the material composing those particles. This difference in emission is related to the ablation process, wherein mass removal occurs and can occur even if the properties of the ablation laser remain constant [17]. It is important to recognize that such limitations exist not only in LIBS but also in other analytical techniques. Despite these limitations, LIBS has demonstrated its efficacy as a powerful tool across various applications [17,21,38,130,139,140]. Furthermore, there are methods available to compensate for the inconsistencies introduced by the matrix effect. For instance, one approach is capturing multiple shots and adjusting the analysis algorithm to disregard unrepresentative data. These compensatory measures help mitigate the impact of the matrix effect and enhance the accuracy and reliability of LIBS analysis in the presence of sample-specific variations.

To enhance the accuracy of LIBS analysis, various calibration methods are employed. Two common approaches are the standard addition method and the use of calibration curves. Calibration curves are created by plotting the signal intensity against the concentration or mass of the analyte, providing a basis for quantitative analysis. Figure 9 illustrates two typical calibration curves generated for different pulse energies. In an ideal scenario, the relation between intensity and mass would be linear for all mass values, with the linear extrapolation passing through the origin. However, in practice, deviations from linearity can occur [17]. Non-linear behavior may arise at the extreme ends of the concentration axis, indicating the effect of analyte concentration on the sensitivity of LIBS. Such situations can lead to a loss of sensitivity, influenced by factors including interference between spectral lines of contaminants and the analyte [17]. False positives may occur

when the concentration of the analyte decreases while the concentration of impurities remains constant. It is important to note that these calibration curves and methods help establish a correlation between the LIBS signal and the analyte concentration, enhancing the accuracy of quantitative analysis. However, careful consideration should be given to potential non-linearities and interferences that may impact the reliability of the results, particularly in situations involving low analyte concentrations or the presence of interfering substances. Rigorous calibration procedures and validation steps can help address these challenges and ensure the accuracy of LIBS analysis.

Another widely used calibration method is the standard addition method, which mitigates the matrix effect effectively. In this approach, a known quantity of the analyte is added to the sample to simulate samples with unknown analyte concentrations [49,50]. The matrix effect is naturally eliminated by utilizing the same sample for calibration and analysis. However, implementing the standard addition method can be time-consuming when dealing with a large number of samples. As a result, extensive research has been conducted to develop calibration-free LIBS methods.

Calibration-free LIBS aims to overcome the matrix effect in quantitative analysis without relying on calibration standards [51,52]. This concept holds significant promise, as it enables real-time, cost-effective, in-situ analysis. Calibration-free LIBS has found applications in various fields, including metal analysis, soil analysis, and environmental monitoring [37,38,51]. The research field dedicated to calibration-free LIBS is thriving, as evidenced by the substantial number of publications on this topic alone in the Web of Science, with around 40 publications in 2021 [51]. The future of calibration-free LIBS appears promising, given the increasing interest and contributions from researchers. Its

potential for real-time analysis, cost-effectiveness, and on-site applications makes it an attractive avenue for further exploration and advancement in the field of LIBS analysis. Continued research and development in calibration-free LIBS hold great potential to revolutionize analytical techniques and expand the possibilities for various industries and scientific disciplines.

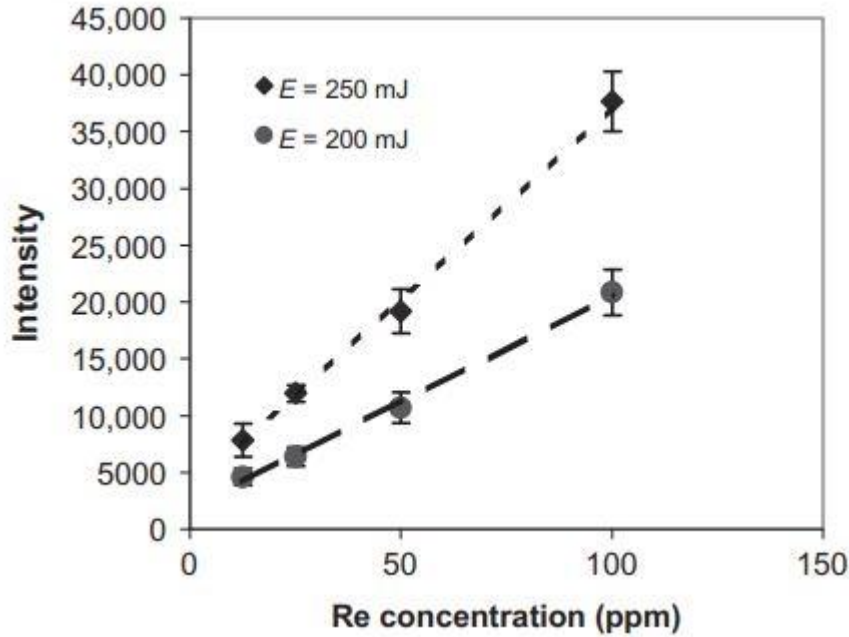


Figure 9 Typical calibration curve. Adopted from [52]

To further enhance the accuracy of LIBS, additional measures can be employed, such as utilizing a double-pulsed laser setup. While LIBS can be performed with a single-pulsed configuration, there are certain applications where a double-pulsed system offers distinct advantages [17]. In a double-pulsed setup, two laser emitters are synchronized so that the second laser pulse impacts the target a few nanoseconds after the first pulse. Researchers have widely reported this configuration enhance the LIBS signal used for sample analysis, although the exact mechanism behind this enhancement is not yet fully understood [24,43]. Several theories have been proposed to explain the signal intensity increase observed in

double-pulsed LIBS. One theory suggests that the enhanced signal is attributed to an increase in the rate of mass removal from the sample surface induced by the successive laser pulses [24]. This notion is supported by the findings of a study conducted by [141], which reported an increased mass removal rate with a delay between laser pulses ranging from 30 to 150 nanoseconds. Additionally, [142] suggests that an optimal delay of 100 nanoseconds is recommended for the detection of atomic lines, while a delay of 3 microseconds is more suitable for the detection of ionic lines. The utilization of a double-pulsed laser setup holds promise for improving the performance and sensitivity of LIBS analysis. Although the exact mechanism behind the signal enhancement requires further investigation, the empirical evidence and potential benefits make it a promising avenue for advancing the capabilities of LIBS in various applications. Continued research and exploration in this area will contribute to unlocking the full potential of double-pulsed LIBS and its impact on analytical techniques.

2.3.2 Sample heterogeneity

Concrete is a heterogenous material and this can make the LIBS analysis more difficult because LIBS performs point analysis. In certain analysis and testing methods, sample preparation is often necessary to ensure the homogeneity of the tested sample. However, in the case of laser-induced breakdown spectroscopy, strict sample preparation is not required sample preparation is not strictly required. [17]. Nonetheless, testing the sample as it is without proper consideration of its homogeneity can yield erroneous results, especially for solid samples. Unlike gases and liquids, solids can exhibit various forms of non-uniformity. Such inconsistencies have the potential to affect LIBS outcomes since it is a point analysis method. If the selected spot for testing is non-representative of the overall

sample, it can lead to incorrect conclusions regarding its composition. Therefore, it is essential to account for sample heterogeneity and carefully choose representative spots for LIBS analysis to ensure accurate and reliable results. This is of relevance in concrete analysis as the properties of the binder (and not the aggregate) are usually of primary interest especially in chloride-induced corrosion analysis [1,69,81].

There are two types of non-uniformity that can adversely impact LIBS analysis: bulk non-uniformity and non-representative surface composition [21]. Bulk non-uniformity is commonly encountered in materials like concrete, where the concentration of constituents within a unit volume may vary even within the same concrete mix. The effect of concrete heterogeneity on LIBS spectra, calibration curves, and LOD has been investigated experimentally in [143] where cement paste, mortar, and concrete samples have been tested using LIBS and the effect of increased heterogeneity was expressed in various ways. For example, Figure 10 shows the dispersion of the normalized calcium readings from the LIBS analysis in the three samples. The paper specifically considered two cases for the concrete under analysis: concrete contaminated with sulfate and chlorinated concrete. The criterion to evaluate the calcium ratio has been selected in accordance with the appropriate spectral lines of Ca and O. It is clear in Figure 10 that the readings are consistent along the cement paste samples, but they become rather erratic as the heterogeneity increases. This heterogeneity has been shown to reduce the accuracy of sulfate detection in the same paper where, similar to the Ca/O ratio, the readings varied greatly when coarse aggregates were introduced to the cement matrix. The presence of aggregate negatively affected the accuracy of the calibration plot of concrete, but the paper also conducted a more sophisticated analysis in which the concrete heterogeneity was taken into account using the

Ca/O ratio and the uncertainty was reduced. Figure 11 shows a spatially resolved 30 mm x 50 mm concrete surface to help explaining the relationship between the Ca/O ratio and the presence of aggregate. This is helpful in chlorine detection as well as the critical dosage of chloride might be greater or lower than LOD depending on whether the total mass or cement mass is considered [143].

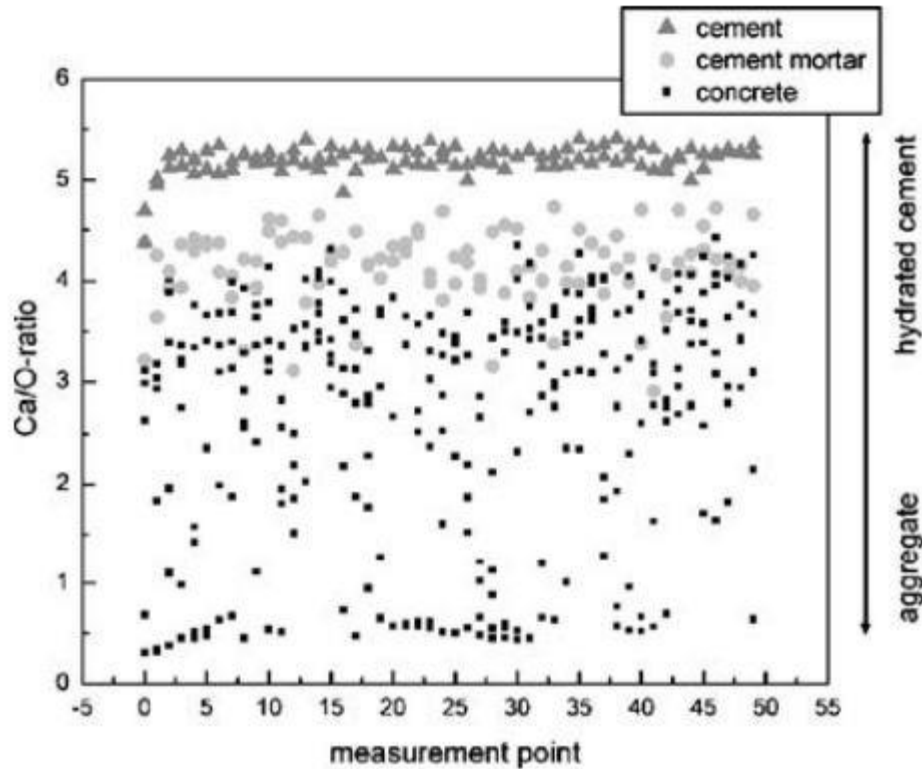


Figure 10 Normalized dispersion of Ca in concrete samples. Adopted from [53].

Luckily, cement manufacturers strive to achieve consistent mixtures, and even if non-consistent samples are encountered, averaging the results from multiple readings can provide a representative measure of the sample composition. This can not be applied with a reliable accuracy to concrete samples mainly due to the presence of coarse aggregate. Yet, phase separation and data segregation can be done using machine learning. In [144], an aggregate extraction model based on k-Nearest Neighbor (KNN) algorithm. Logistic

regression, Decision Tree Classification, Ridge Classifier, and Random Forest Classifier where all considered, but KNN showed the best results in this particular case. The usage of this model can be computationally expensive and require a wide domain of knowledge, but it is a good choice in applications where accuracy is favored over frequent predictions [145]. Four elements taken into account while developing the model: calcium, carbon, hydrogen, and oxygen. These elements were selected to avoid self-absorption, over-saturation and line overlapping; oxygen also contributes to the normalization process as environmental factors can introduce deviations in LIBS signals. Aggregate samples with in epoxy resin medium, cement, and concrete specimens were used to train the model and the final results were cross-validated with other algorithms. The paper claims that the developed model can distinguish between cement and aggregate with almost 100% accuracy.



Figure 11 The distinction between aggregate and cement was done using LIBS and the results are graphically presented above. Adopted from [140].

The other type of non-uniformity, non-representative surface composition, is observed in certain metals and rocks, where the surface composition differs from the bulk composition. This phenomenon can be seen in metal alloys when impurities rise to the surface as the molten metal cools down or in rocks where desert varnish, an Mn-rich layer, forms on the surface in arid environments [21,146]. Multiple shots can be taken from the same spot during LIBS analysis to address this effect. By ablating (removing) the surface with successive laser shots, the underlying bulk material is exposed for analysis. Figure 12 illustrates the impact of non-representative surface composition, where multiple laser shots remove the Mn-rich surface layer, revealing a bulk composition with significantly less Mn. The figure also demonstrates the inconsistency in Si measurement for this specific sample. To account for these discrepancies, multiple spots can be tested with multiple shots, or if feasible, a well-mixed sample can be prepared and analyzed. By being aware of these non-uniformities and employing appropriate strategies such as multiple shots or well-mixed samples, the reliability and accuracy of LIBS analysis can be enhanced, enabling more representative assessments of material compositions.

2.3.3 Lens-to-sample distance

As mentioned previously, in LIBS, a setup of lenses is utilized to focus the laser beam and generate plasma on the sample surface. However, it is important to note that plasma formation can still occur even if the distance between the lens and the sample deviates from the focal length of the lens. This variation in the lens-to-sample distance (LTSD) can lead to changes in the amount of material ablated, subsequently affecting the emission signals [21]. While controlling the LTSD is feasible in a controlled laboratory environment, it can pose challenges in industrial applications, such as when analyzing samples on a conveyor

belt. Fortunately, there are several strategies to address this limitation. One approach involves using a lens with a long focal length, where the changes in LTSD become insignificant [17]. This helps to minimize the impact of fluctuations in the lens-to-sample distance on the ablation process and subsequent signal generation. Another solution is employing a system of adjustable lenses. This adjustable lens system allows for precise focusing of the laser beam on the sample, accommodating variations in the LTSD encountered in industrial scenarios. By implementing these approaches, the potential errors associated with changes in the lens-to-sample distance can be mitigated, enhancing the accuracy and reliability of the LIBS analysis, particularly in practical industrial applications where maintaining a constant LTSD may be challenging.

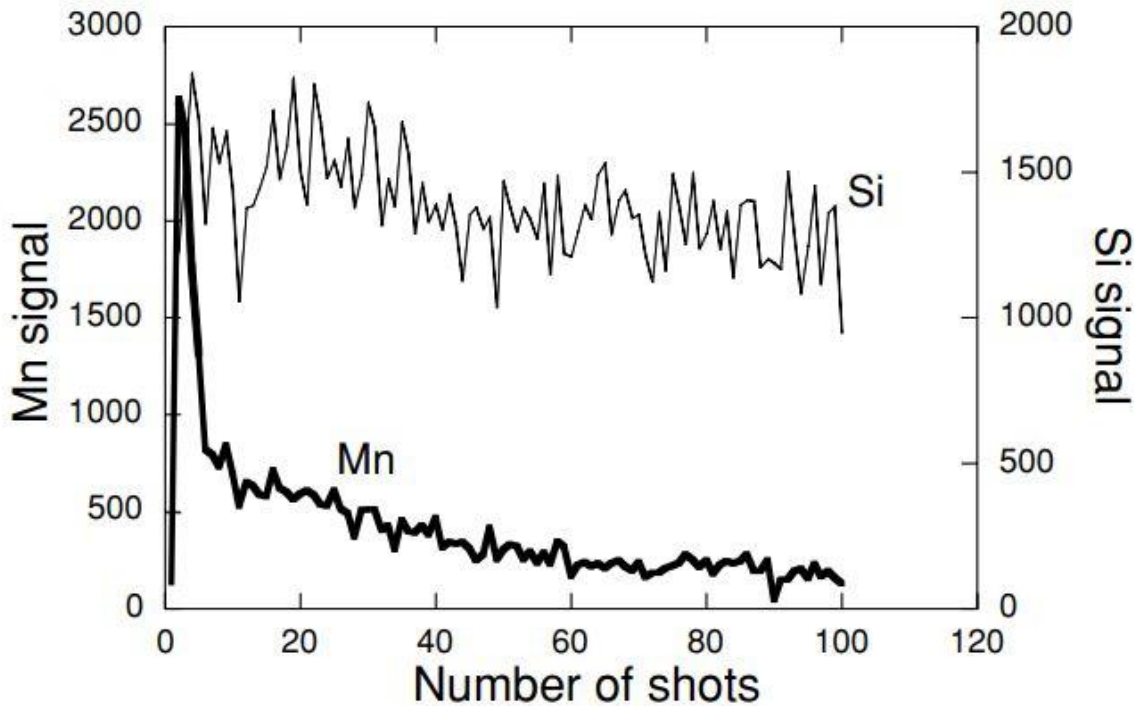


Figure 12 The impact of non-representative surface composition where the first shots (ablating the surface) indicate a high concentration of Mn. Adopted from [37].

2.4 LIBS as a tool to analyze materials at different states of matter

Few analytical methods have ever sparked as much attention within the analytical world as LIBS has. The physics and chemistry literature has produced important papers on experimental and theoretical aspects of laser breakdown in gases, liquids, solids, and aerosols, modeling of laser-induced breakdown and ablation on solids [147–149].

2.4.1 Granular and fine materials

LIBS has emerged as a valuable tool in various soil analysis applications. One significant use case is the detection of heavy metals in soil, where LIBS has greatly streamlined the testing process [137]. Traditionally, soil analysis involves several steps, including sample collection, transportation, dissolution, and analysis using different techniques. However, with LIBS, none of these initial steps are required, presenting a major advantage for the easy detection of heavy metals in soil. This application is crucial because heavy metals in soil can pose environmental and health risks [150].

The application of LIBS in soil analysis extends beyond the detection of heavy metals. It has also been used to identify other elements such as iron, potassium, zinc, and more, which is important as some substances in soil, apart from heavy metals, can also be toxic, including pesticides, batteries, and paints [137,150]. Additionally, LIBS has proven effective in determining other key soil parameters such as pH, total potassium, and soil organic matter [136]. While alternative methods exist for assessing these parameters, they are often labor-intensive, time-consuming, and expensive. With proper calibration, LIBS can surpass conventional soil analysis methods in several aspects despite its inherent drawbacks, like the matrix effect. Furthermore, recent advancements in calibration-free LIBS further enhance its appeal as a fast and cost-effective analytical technique. From an

engineering standpoint, LIBS holds promise in soil analysis as it allows for inferring the physical properties of soil based on its composition [37]. Moreover, the presence of specific elements like sulfate or chloride is of great concern to civil engineers, and LIBS has been repeatedly utilized to detect and analyze such elements [41–44,46,151,152]. This capability provides valuable insights for engineers involved in soil characterization and the design of structures and foundations. LIBS's versatility and its ability to provide rapid, non-destructive, and comprehensive analysis make it a promising technique for soil analysis across various disciplines.

2.4.2 Liquids and slurries

Analyzing fresh concrete in its liquid state can be useful, but there are some difficulties regarding the analysis of liquid matters using LIBS. However, the analysis of liquid and slurry samples using LIBS has been an active area of research, driven by the challenges associated with analyzing these sample types [35,41,148]. These challenges include issues like liquid splashing, bubble formation, and the inherent inconsistency of certain slurry samples. To overcome these challenges, researchers have adopted various approaches. For instance, some have conducted LIBS analysis of liquids in closed glass bottles following liquid setups [41]. Another approach involves coating an aluminum target with the liquid analyte and subsequently performing the analysis. Additionally, a solution proposed by [148] involves precipitating the liquid sample to reduce its water content prior to analysis. While liquid samples pose challenges when analyzed using LIBS, the aforementioned solutions hold promise in addressing these difficulties. Continued research and development in this area are crucial to further enhance the capabilities and reliability of LIBS for liquid and slurry sample analysis.

2.4.3 Analyzing pure cement

LIBS analysis has also found application in the analysis of fine materials, such as glass batches. In the glass manufacturing industry, a mixture of elements, including limestone, barite, and silica sources is pulverized into a fine powder [153]. This powdered material can be further processed by melting it to create glass or packaged and transported as batches for processing at another location, similar to cement batches. LIBS analysis has emerged as a valuable tool for analyzing these glass batches [139], providing insights into their elemental composition and ensuring quality control through the manufacturing process. By harnessing the capabilities of LIBS, the glass industry can optimize its production processes and maintain consistent quality standards in glass batch compositions.

LIBS has emerged as a valuable technique for analyzing cement in various ways. One application is the analysis of constituents in hardened concrete, which allows for determining the cement type used in the mixture [154–157]. Moreover, preliminary studies have indicated that LIBS holds the potential to determine other properties of hardened concrete beyond just the cement type [154]. For instance, LIBS can potentially identify the aggregate type and content, an important aspect of ensuring concrete quality and compliance with design code requirements. Another study focused on analyzing hardened concrete samples taken from a concrete dam to assess their composition and evaluate any potential environmental risks associated with the materials used in its construction [158]. In this study, the reliability of LIBS was further validated by comparing its results with those obtained from another analytical method, Laser Ablation Time of Flight Mass Spectrometry (LA-TOF-MS). The concordance between the two methods reaffirmed LIBS' efficacy in concrete analysis [158].

Nevertheless, analyzing concrete samples with LIBS can be challenging due to the heterogeneous nature of concrete, particularly the presence of coarse aggregates. To address this issue, a method proposed in [144] aimed to differentiate between aggregate and cement paste in LIBS analysis to mitigate inaccuracies arising from concrete heterogeneity. This approach employed machine learning algorithms, commonly utilized in conjunction with LIBS due to the complexity of the analysis [36,117–121,159–161]. The study emphasized the challenge posed by the similar chemical composition of cement and commonly used types of aggregate [92,162,163], making their distinction difficult using conventional chemical methods. By leveraging machine learning, the developed model achieved an impressive accuracy rate of nearly 100% [144]. Machine learning, being a data-driven method, can be integrated with LIBS for materials investigation [164–167]. These findings highlight the potential of combining LIBS with advanced data analysis techniques to overcome the complexities associated with concrete analysis and enhance its accuracy and reliability.

The analysis of powdered cement holds significant importance given its widespread use, estimated at 10 billion tons per year globally in 2020 [168]. LIBS has proven to be a valuable technique for conducting such analyses.

2.5 LIBS as a tool to assess corrosion of reinforced concrete structures

2.5.1 Detection of chloride ions

LIBS has emerged as a promising method for assessing rebar corrosion in concrete structures by detecting elements responsible for corrosion, such as chloride, within the concrete matrix. Elemental detection is a primary objective of LIBS, and its application in

detecting corrosion in reinforced concrete structures has yielded successful results. In a study by [43], LIBS was employed to identify chloride using two emission lines. Various spectral intensities were investigated to mitigate the impact of self-absorption, a phenomenon in which light emitted from one atom is absorbed by another atom in the same matrix. In concrete, for instance, calcium oxide tends to absorb the emitted light from chloride, necessitating the use of a dual-pulsed laser system to detect chloride through a different emission line [43]. The accuracy of this approach was deemed acceptable, as the limit of detection of 0.2% fell within the allowable chloride limit for many structural applications [2]. These findings align with the study by [135], where the limit of detection for all concrete elements, including chloride, was determined to be approximately 0.1%. The measurement precision for chloride content in cement paste was explored by [169], who engaged 12 laboratories across 10 different countries to perform LIBS analysis on samples with chloride concentrations ranging from 0.06% to 1.95% by weight. Notably, no specific instructions regarding the testing methodology were provided to the technicians. Despite this, the margin of error observed in the chloride content measurements was less than 15%. These results emphasize the reliability and reproducibility of LIBS analysis in determining chloride content in cement paste.

In a related study by Zhi et al., a dual-pulsed LIBS approach, similar to the one employed in [43], was used to measure chloride in cement paste quantitatively [170]. The study reported a limit of detection of 103.4 ppm for the two-nanosecond dual-pulsed laser setup, which utilized energy equivalent to 30 mJ. Notably, this limit of detection differs significantly from those reported in [43] and [171]. Furthermore, the study provided detailed technical parameters for the setup, enhancing reproducibility and enabling its

application in similar experiments if desired. For instance, the inter-pulse delay was set at 2000 ns, and the gate delay at 800 ns. To improve the signal-to-noise ratio (SNR), an essential factor affecting the accuracy of LIBS, the study employed optimization techniques. Addressing this issue, M. A. Wakil and Zeyad T. Alwahabi specifically investigated the use of microwaves to enhance the SNR in their work [22]. This approach, widely utilized in SNR enhancement efforts [22,25,68,132–134,146], yielded impressive results. According to their findings, the limit of detection for chloride on cement surfaces improved by a factor of 10, resulting in a limit of detection of 47 ppm. This value is lower than the limits reported in [43] and [170] and well within the allowable chloride concentration for concrete structures [2]. The utilization of microwaves to enhance SNR represents a promising avenue for improving the accuracy and sensitivity of LIBS analysis for chloride detection in cement-based materials [133,172,173].

Another relevant study conducted by J. Mateo et al. focused on the detection of chloride using LIBS in mortar samples, as opposed to cement paste [23]. The research involved subjecting the mortar samples to seawater for a period of 5 years to simulate harsh exposure conditions. Traditional chemical and LIBS analyses were performed to determine the chloride concentration. The study also provided insights into the optimal setup details for using LIBS in this context. Specifically, a 320 mJ Nd: YAG laser operating in a helium medium was employed to detect the 837.6 nm chloride line. It is worth noting that other researchers, including those in [170], have utilized the same type of laser (Nd: YAG), albeit with different laser energy levels (30 mJ in [170]). The results obtained using the setup described in [23] demonstrated accuracy and efficiency, surpassing traditional chloride

detection methods. Furthermore, the study highlighted the potential of utilizing LIBS as a portable device for in-situ measurements of chloride in concrete structures.

While the previously mentioned papers primarily focused on determining chloride concentration, another study by [44] delved into investigating the diffusion of chloride in mortar and concrete samples. This research employed a basic LIBS setup with a 320 mJ Nd: YAG laser in a helium chamber. The objective was to indirectly determine the chloride diffusion coefficient and map the distribution of chloride ions, moving beyond the assessment of concentration alone. The samples in [44] were subjected to a salt solution for durations of 3, 6, 30, and 60 months, followed by LIBS analysis. The obtained results exhibited reasonable agreement with Fick's second law of diffusion and provided diffusion coefficients within the range reported in other studies, such as [90,174–178]. This work expanded the application of LIBS in studying the behavior of chloride ions and their diffusion properties in cementitious materials.

LIBS has demonstrated its effectiveness in evaluating protective techniques against rebar corrosion. In studies such as [152,179], LIBS was employed to monitor the movement of chloride ions resulting from a chloride extraction method applied to reinforced concrete samples. The chloride extraction involved the use of a zinc anode embedded in the specimen, a common protective technique [180–185]. This approach establishes an electrical circuit where the steel rebar is connected to the anode, causing the migration of chloride ions from the rebar to the anode due to the applied electrical current [1]. In [152], an embedded zinc anode was utilized to induce the migration of admixed chloride ions from the cathode to the anode over the course of one year, while LIBS was employed to

record the chloride ion concentrations. The results demonstrated the effectiveness of this protection technique, as the chloride concentration was significantly reduced.

LIBS analysis has also exhibited high accuracy in determining free chloride ions in blended cement [42], which is particularly relevant due to the prevalent use of admixtures in cement compositions [186–188]. The study involved testing a total of 55 samples with seven different mix proportions, considering variables such as the water-to-cement ratio and the type of admixture. LIBS analysis was conducted, followed by the determination of actual chloride ion concentrations using titration. The variation between the results obtained through LIBS analysis and titration was found to be a mere 0.05% by weight. This demonstrates the reliability of LIBS as an analytical method for quantifying chloride ions in blended cement, enabling accurate assessment of chloride ion content and its potential impact on corrosion susceptibility.

2.5.2 Detection of sulfate ions

Sulfate is recognized as a significant contributor to concrete deterioration [92], although its impact on rebar corrosion is not substantial unless it is accompanied by chloride [12]. In such cases, the presence of sulfate can double the corrosion rate caused by chloride in concrete [12]. Therefore, detecting sulfate is crucial for assessing corrosion in reinforced concrete structures. In [24], the concentration of sulfate in a concrete sample was successfully detected using LIBS, with a determined limit of detection of 38 µg/g. Another study focused on a repaired concrete structure where a repair mortar was applied to the surface [189]. The objective of the test was to verify the adequacy of the mortar cover's depth. LIBS was employed to generate a color-coded map illustrating the penetration of sulfuric acid, as Figure 13 shows. Unfortunately, the repair work was found to be

inadequate, as the old contaminated concrete was not fully replaced. It is worth noting that sulfuric acid can react with rebar, leading to the formation of ferrous sulfate [12].

Detecting non-metals poses certain challenges due to their high limit of detection [190–192]. Consequently, specific research efforts have been dedicated to improving the detection of non-metals, including sulfur in concrete samples. For instance, in [190], a 532 nm LIBS system was optimized for the detection of sulfur in concrete samples within a helium chamber. The study investigated the effects of gate delays and signal-to-noise ratio (SNR) on the 921.29 nm sulfur emission line. Concrete samples containing 0.43% to 0.61% sulfur were analyzed using the described setup, yielding sulfur content measurements ranging from 0.41% to 0.70%. This indicates that LIBS can be utilized, at least in preliminary surveys, for the detection of sulfur, considering that the allowable sulfur limit in certain codes, such as [3], is 0.60%. It should be noted that some sample preparation was conducted prior to the test, involving grinding the concrete specimens into powder and subsequently pressing them into pellets. While sample preparation is not strictly necessary, field tests conducted without sample preparation may yield less precise results. Nonetheless, LIBS remains a promising tool for detecting contaminants in concrete due to its versatility. Apart from determining element concentrations, as discussed earlier, LIBS can generate accurate continuous ingress profiles of contaminants along a given sample [45,46,193]. This mapping technique was employed in [193], where a depth profile of sulfur was obtained using LIBS and compared with chemical analysis results. In addition to its accuracy and speed, LIBS offers the advantage of providing continuous depth profiles, as depicted by the black line in Figure 14, unlike traditional chemical analysis methods.

2.5.3 Detection of rust products

In [194], a more direct approach was employed to detect rebar corrosion using LIBS. Instead of focusing on detecting the contaminants responsible for corrosion, the study utilized LIBS to detect corrosion products such as iron, manganese, and chromium. This approach proves valuable when the concentration of contaminants falls below the limit of detection of LIBS, which is more common with handheld devices that lack signal amplification [18,19,170,194,195]. Consequently, the study in [194] analyzed the signals of corrosion products present on the surface of concrete. Readings were obtained using LIBZ-200, a handheld LIBS device, specifically on the areas covered with rust stains, where the signals were found to be reliable.

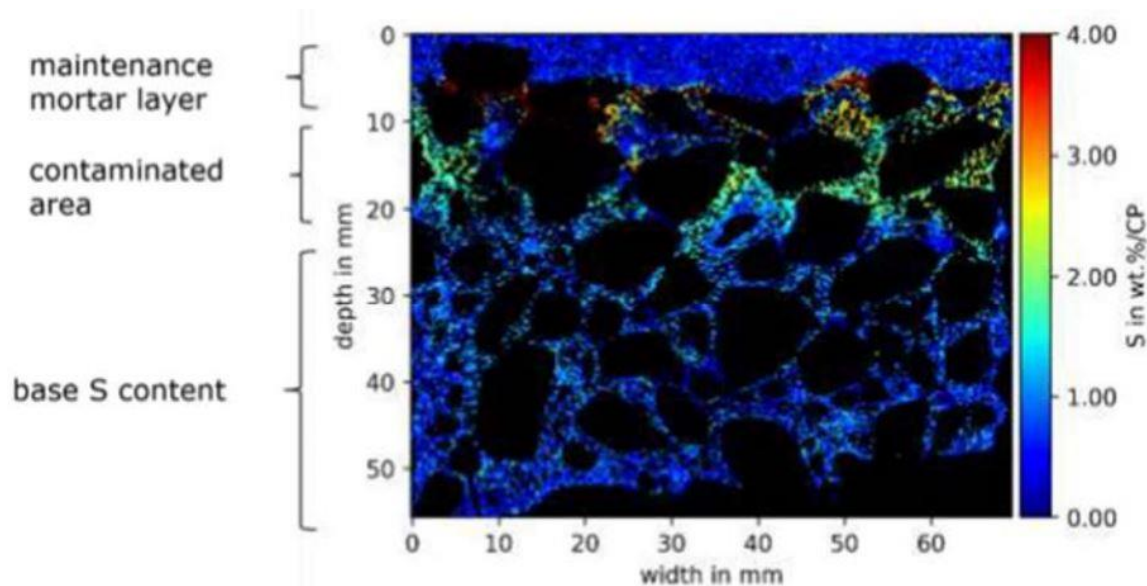


Figure 13 The penetration depth of sulfate (in blue) in a concrete member. Adopted from [69].

Notably, the same LIBS setup has been used in various studies to determine chloride concentration, chloride diffusion coefficient, sulfate ingress profile, and the concentration of rust products in cement, mortar, and concrete. This highlights the versatility of LIBS, which is a significant factor that attracts scientists to this analytical technique. Furthermore,

the aforementioned studies reported favorable agreement between the results obtained from well-established traditional testing methods and LIBS. Based on these findings, it can be inferred that LIBS may potentially replace conventional cement testing methods in the near future or, at the very least, become a standard method alongside existing approaches for cement testing.

2.5.4 Potential use of LIBS to analyze fresh concrete

Testing concrete before the final casting is very common practice in the field of civil engineering and even though a strict quality control is usually maintained in concrete mix plants, there is no technology that can insure a perfect final product. Thus, quality tests are sometimes done as a check to ensure that the patch delivered to the site meet the requirements of the job. However, only basic tests are done on site, such as the slump test, where compositional analysis is not. This is where handheld LIBS could be useful; to analyze concrete in its liquid state and determine the quantities of additives or contaminants, for example. The analysis of liquid and slurry samples using LIBS has been an active area of research, driven by the challenges associated with analyzing these sample types [35,41,148]. These challenges include issues like liquid splashing, bubble formation, and the inherent inconsistency of certain slurry samples. To overcome these challenges, researchers have adopted various approaches. For instance, some have conducted LIBS analysis of liquids in closed glass bottles following liquid setups [41]. Another approach involves coating an aluminum target with the liquid analyte and subsequently performing the analysis. Additionally, a solution proposed by [148] involves precipitating the liquid sample to reduce its water content prior to analysis. While liquid samples pose challenges when analyzed using LIBS, the aforementioned solutions hold promise in addressing these

difficulties. Continued research and development in this area are crucial to further enhance the capabilities and reliability of LIBS for liquid and slurry sample analysis. However, no comprehensive research, according to our knowledge was done to evaluate the potential use of handheld LIBS on constructions site to determine the quantities of contaminants or additives.

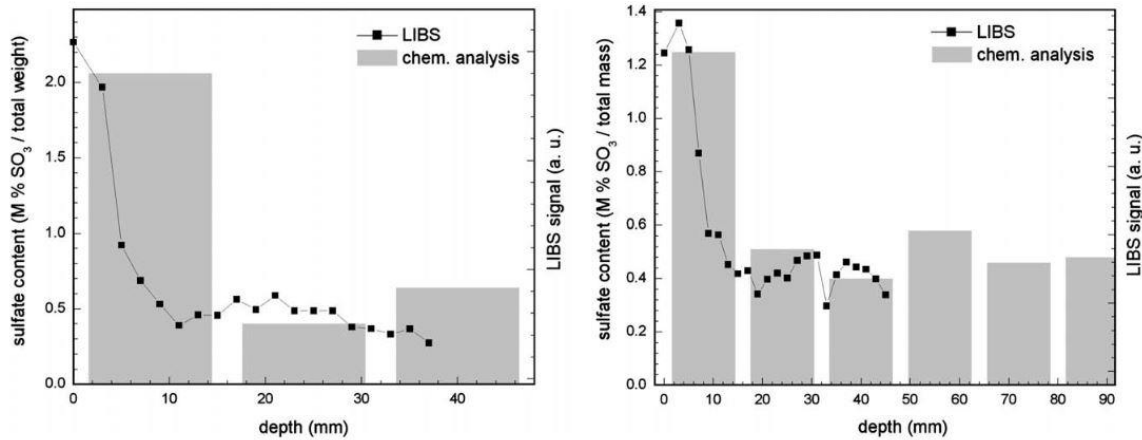


Figure 14 A demonstration of LIBS ability to generate a continuous contaminant profile. Adopted from [99].

In summary, this chapter has presented the recent developments and challenges associated with using Laser-induced breakdown spectroscopy (LIBS) for corrosion assessment in reinforced concrete structures. The findings have shown that LIBS is a fast, reliable, and cost-effective method for detecting corrosion, particularly with the use of handheld LIBS devices that offer flexibility and portability. Furthermore, the integration of LIBS devices with online monitoring systems, such as the Internet of Things, can provide real-time corrosion rate data transmission for efficient monitoring. The review chapter has emphasized the importance of establishing strong correlations between LIBS data and other material characteristics, as well as identifying the most sensitive emission lines for accurate detection. Appendix A also summarizes the reviewed literature. Dual-pulsed laser configurations have demonstrated reliable results in corrosion assessment. Although

challenges such as limits of detection, repeatability issues, matrix effects, and other obstacles still exist, various approaches and solutions have been discussed to address these limitations. The potential of LIBS as a quantitative analysis technology in engineering fields, including corrosion engineering, holds great promise. As further research and advancements continue, LIBS has the potential to become a valuable tool for corrosion detection and monitoring in various applications.

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 Overview

In this study, concrete cubes and cylinders with embedded rebar were cast from the same concrete patch. Afterward, the cubes were tested using LIBS (Q-switched Nd:YAG at 1064 nm), and the cylinders were subjected to accelerated corrosion. Then, the rebar inside the cylinders was extract-ed to conduct a gravimetric analysis. A correlation between the output of LIBS, that is the chloride concentration, and rust formation rate was then developed. Common additives, illustrated in Table 1, along with the targeted weight loss degree, were chosen because they are used very frequently nowadays.

3.2 Experimental work

3.2.1 Sample preparation

Two types of cement were considered in this work: Type I (ordinary) and Type V (sulfate resistant). The former was considered because it is considered as a benchmark to compare the other types with and the latter was chosen because it is more prone to chloride-induced corrosion due to its low C3A content. In addition, the action of sulfate and chloride is usually studied together because they have a synergetic effect and some areas, such as the coastal regions in Saudi Arabia, are contaminated with both chloride and sulfate. Three pozzolanic materials were considered as well. Specifically, fly ash, silica fume, and ground granulated blast-furnace slag were added at 30%, 50%, and 7% respectively, which are the typical dosages for these materials. The addition of pozzolanic material was important

because they are used heavily nowadays. A control sample with no additives was prepared as well. Furthermore, five different concentrations (0%, 0.1%, 0.4%, 0.7%, and 1% by weight of cement) of the contaminant, which is sodium chloride, were tested. It is true that the concentration is somewhat on the higher side when compared to the allowable dosage of chloride in reinforced concrete structures (which can be as low as 0.2% by weight of cement [7]), but these values were selected carefully based on previous studies to ensure that LIBS can detect the chloride ions and to easily spot the effect of increasing the chloride. Also, the corrosion degree was set to be at about 9% and 18% for each sample, measured using gravimetric analysis. The de-sired corrosion degree was achieved by trying many different combinations of exposure time and corrosion current density. The dosages of the selected additives were based on the literature, as Table 2 shows. Also, the chloride concentrations are in the range of the allowable dosages in concrete structures. The maximum allowable chloride dosage in different concrete structures is shown in Table 3.

Table 2 The variables in the experimental program

Variable	Value
Cement types	Type I and Type V
Additives	None, GGBFS (50%), SF (7%), and FA (30%)
Chloride concentration (by weight of cement)	0%, 0.1%, 0.4%, 0.7%, and 1.0%
Degree of corrosion	None, 4V for 5 days, and 8V for 5 days

Table 3 Common additives in concrete with their typical dosages

Additive	Typical %	Ref
SF	10%	[32]
FA	30%	[33]
GGBFS	50%	[34]

Table 4 Max chloride dosages in concrete structures

Concrete use	Maximum Cl% by mass of cement
Plain concrete	1.0%
Reinforced concrete	0.4%
Prestressed concrete	0.2%

200 by 100 mm concrete cylinders with an embedded steel bar were prepared to be subjected to accelerated corrosion. This type of sample is known as a lollipop sample. The tip of the embedded section of the bar as well as its top were covered with Sika's MasterEmaco 8100 epoxy to restrict the corroded area. The casting and demolding were then carried out in a typical manner. The samples were corroded by connecting them to a DC PSU for various amounts of time at different voltages. The samples were placed in a salt-based solution and confined with counter electrodes. 50 mm cubes were also cast from the same batch to measure the concentration of chloride and the corresponding signal using LIBS. Lab-grade sodium chloride was added to the mixing water before it was poured into the concrete mixer. The lollipop specimens were then subjected to accelerated corrosion. A typical accelerated corrosion setup composed of a 15V (max) DC PSU, single-core

wires, alligator clips, data cables, 3-sided counter electrodes, and copper distributes was used. The samples were submerged halfway into a 5% salt-based solution and the negative PSU terminal was connected to each counter electrode. The positive terminal was connected to each sample through a distributor. The samples were subjected to current-induced corrosion to accelerate the process of rusting, otherwise this process might take years. This is a common practice in corrosion studies [35–40]. However, applying excessively high current can cause pitting corrosion and thus fail to simulate a real-life situation of rebar corrosion [7,40]. In this particular experiment, trial samples were made to calculate the theoretical corrosion current density before conducting the actual tests. The current density was less than the limit suggested by G. Malumbela ($1000 \mu\text{A}/\text{cm}^2$) for a valid simulation of a real rebar corrosion situation [40].

3.2.2 LIBS setup

The setup of the LIBS system is shown in Figure 15 and Figure 16. It has been used before in many studies [26,41–44]. It consists of an Nd: YAG laser pump (from Big Sky Laser), which is capable of delivering 1 J of energy at its peak with a pulse width of 8 ns and 10 Hz repetition rate in Q-switched mode. The laser source was operating at 1064 nm (fundamental) and has been used for plasma generation. Further, the laser energy was calibrated by an energy meter (from Ophir Optics Inc.). Also, a spectrometer (from Ocean Optics LIBS 2000+), a moving platform, and a focusing lens. OOLIBS software was used to record the readings. The pulse energy range in this experiment was 20 – 60 mJ and the light was collected via a collimating lens. The LIBS setup could provide a high resolution full-width at half-maximum (FWHM 0.1 nm) in the 200 – 800 nm region. A charged-couple device (CCD) camera was attached to the detector to measure and spatially resolve

the spectra simultaneously with high resolution. The spectra were reconstructed from the obtained data using the spectrometer and the connected PC. The setup also includes a 2D stage to place the sample on, which is used to move the sample steadily and accurately using this stage manually or automatically by attaching a motor. The delay between opening the shutter and the laser shot was set to 5 μ s to minimize the interference with bremsstrahlung emissions. The captured emissions were reconstructed by the software that is built-in in the spectrometer and the results were sent to a connected PC. The emission was observed at a 45° angle to the laser spot.

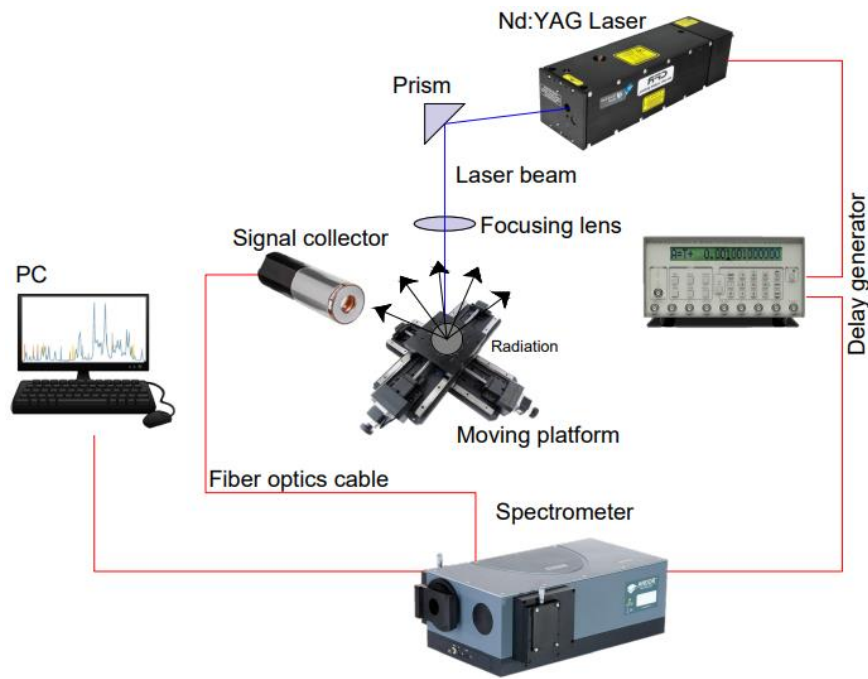


Figure 15 a schematic diagram of the used LIBS setup

It should be mentioned that irrelevant peaks were detected prior to the optimization of the setup. One reason for this is the moisture content of concrete. The noisy signals may also be attributed to the lack of sample treatment i.e. grinding the sample to fine powder. However, the parameters of the setup we have used such as the laser energy, the delay time, and the pulse duration were optimized to minimize this effect as much as possible. This is

a challenging task due to the large number of parameters involved in laser analysis. Our results, nonetheless, were reliable and reproducible and the optimum values for the experimental setup were reported, as mentioned earlier. In short, the spectrometer calibration was done using high-purity (99.99%) powdered metals. The list of these materials includes titanium, iron, aluminum, and copper. Different combinations of powdered metals and potassium bromide (99.99% purity) samples were mixed in a milling machine and tested to calibrate the setup. The results of LIBS were also cross-validated with Coupled Plasma Optical Emission Spectrometry (ICP-ES).



Figure 16 the laser setup while being tested

Table 5 dominant elements

Element	Wavelength (nm)
Si I	288.2
Al I	309.3
Fe II	259.9
Ti II	334.9
Ca II	315.9
Mg I	285.2
K I	769.9
Cl I	594.9
Na II	284.2
Na I	616.1
Ti I	589.9
Ca I	559.4
Ca I	644.9
Ca I	714.8

3.2.3 Experimental procedure

To determine the corrosion degree of the rebar inside the lollipop samples, gravimetric (weight loss) analysis was conducted according to ASTM G1. The results were recorded and the elemental analysis of the cubical samples was then carried out using LIBS. Each sample was placed on the moving platform on its side during the test to avoid the effect of non-representative surface composition that may occur if the samples were over-vibrated and the rising water during the vibration process carried any components to the upper surface. To prevent creating deep cavities on the analyte during the analysis, the concrete samples were placed on the XY moving platform. This is important to maintain high spatial resolution. The sample was moved slowly using a mechanism attached to the platform. This also takes shots at different spots and takes into account the heterogenous nature of concrete. The study aims to simulate casted concrete in buildings as much as possible, that is, avoiding unconventional sample processing. Thus, sample treatment was minimized.

However, normal construction practices, such as vibration, were followed. The spectral data were recorded automatically by the attached PC and the fingerprint of each element (spectral line) and the peaks were assigned according to NIST's spectral database.

The cylindrical lollipop concrete samples were tested using gravimetric analysis to determine the degree of corrosion to obtain the %loss in weight. The exposure time was already set to be five days and the bar area exposed to the chloride action (the area inside the concrete body that is not covered with epoxy) was measured. From these parameters, the rust formation rate was calculated. Figure 17 shows a few samples before and after the corrosion took place.



Figure 17 corroded and uncorroded tests samples

3.2.4 Results and discussion

The dominant elements in the test set were determined by identifying the lines with significant intensities. Figure 18 gives an example of the conducted peak analysis. The considered peaks are shown in Table 5 along with their corresponding wavelengths from NIST. The results from this analysis are relevant because the identified elements are expected to be present in each sample. For example, calcium and aluminum are two important constituents of cement. Thus, these two elements appeared on all spectrums with a high intensity. The results shown on that table are also in agreement with the similar studies done on cement-based materials [41,42,45,46]. Some elements were also detected on different wavelengths. For instance, Ca I was detected at 559.4, 644.9, and 714.8 nm. In addition, some elements were captured at both natural state and ionized state, such as Na I at 616.7 nm and Na II at 284.2 nm.

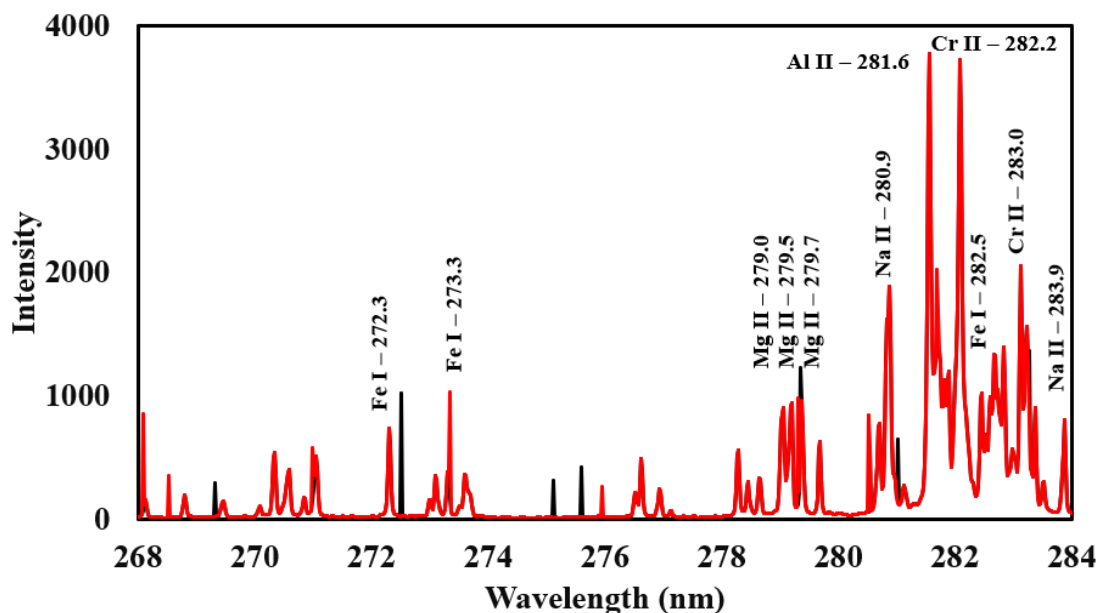


Figure 18 The spectra of two samples with the same composition (one in red and the other in black) shows the results consistency

To show the consistency of the results, a snippet from the obtained wavelength with their corresponding intensities from 2 selected samples is shown in Figure 18 and Figure 19. It is clear that the variation of the signal from different samples is minimal. The slight discrepancies between the samples could be due to the nature of the raw materials or the production process. For example, the locations from which the raw materials might be different and, consequently, the chemical composition of the used cement will differ. It is also worth mentioning that the composition of Type I cement and Type V cement is not the same [47]. Hence, the correlations for those two types might slightly differ. In addition, on some occasions, the variation observed in Figure 18 is just due to the different concentrations of a particular element within the selected samples. For example, Figure 19 shows a zoomed-in section of Figure 18 and it is noticeable that Sample 2 has a slightly higher concentration of the elements in the 271 nm wavelength. This confirms that LIBS was able to detect the same elements, as it should, in various samples but, the slight variation is due to the reasons mentioned earlier. As for the signal of chloride, it was much more significant than the signal of the other elements presented in Figure 20 and Figure 21.

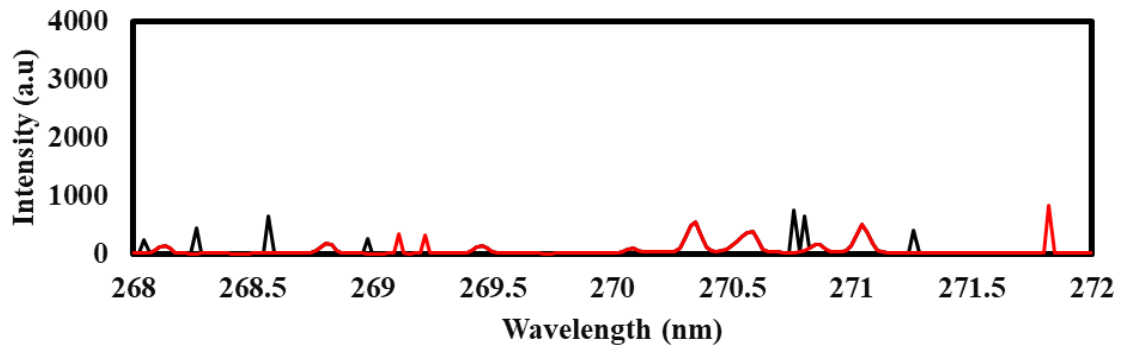


Figure 19 zoomed-in section from Figure 16

After determining the significant peaks and confirming the reliability of the results, further analysis was carried out by comparing the signals of the determined dominant peaks. Figure 6 shows the comparison between different samples with SF. The X-axis on that figure represents various elements from different sample sets and the Y-axis represents its corresponding signal. The most noticeable trend is the variation of Cl intensity with the increase of chloride dosage regardless of the additives or the degree of rebar corrosion, as it should be. There are two instances where the signal obtained from two samples with similar chloride concentrations varied slightly, particularly the 0.7% Cl and the 1.0% Cl. This slight inconsistency is still negligible considering the fact that the samples were tested without any treatment. In addition, pure calcium chloride, with no anti-agglomeration, was used as a contaminant, which might have caused small lumps of chloride to accumulate in some spots. Also, this minor contrariety is only observed at higher Cl concentrations, where the chance of Cl agglomeration increases. This inconsistency, nonetheless, was not observed with the Na I line although Cl and Na are both present in this mix due to the addition of admixed contaminant. This, in fact, should be the norm due to the extensive mixing of concrete prior to the casting. The Na II line, however, seems to be a weak line and no difference in the LIBS signal was observed, under this particular scenario, with the increase of the sodium chloride signal. The concentration of many other elements, such as

silica, iron, potassium, and manganese remained almost constant during the entire test as no change that can affect the concentrations of these elements was made.

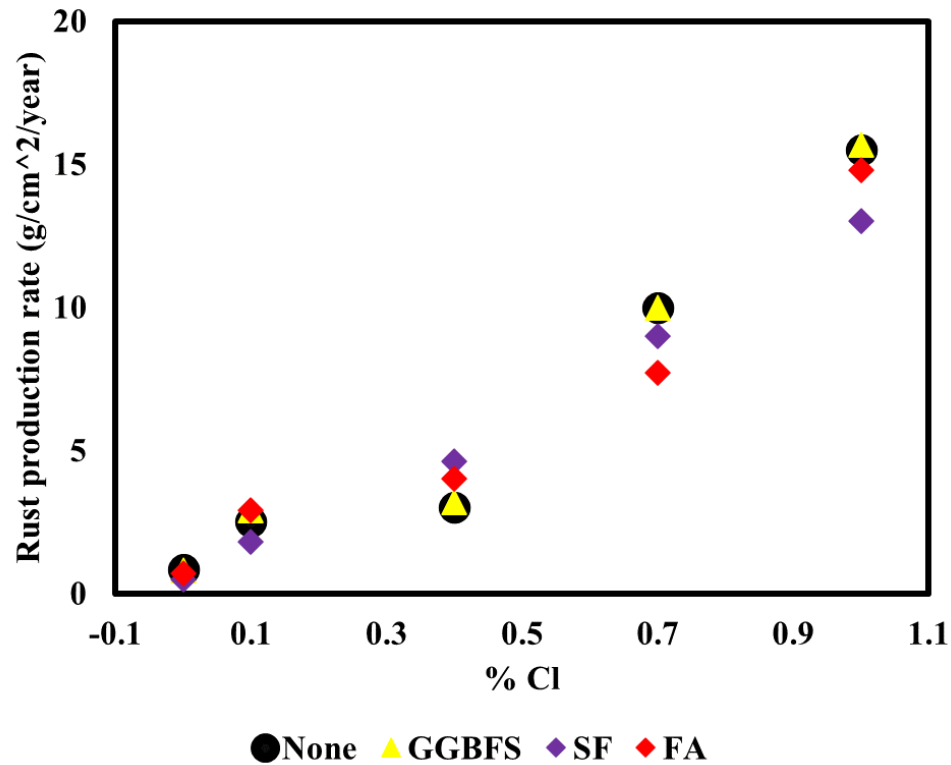


Figure 20 The effect of chloride concentration on rust formation rate for Type V samples

The signal of aluminum, however, was not constant although no extra Al was added to any test specimens. The variation is minor, nonetheless, and it should also be mentioned that this is because this particular LIBS setup was optimized to detect chloride. Thus, a small increase or decrease in the signal of some elements is expected. The signals of the different phases of calcium are also slightly fluctuating and some lines appear to be stronger and easier to detect than others. That is a common trend noticed in many similar researches [31,48–51]. It should also be mentioned that the presence of many lines of a particular element confirms that this sample under analysis contains that element. In contrast, when a single line of an element that has many fingerprint wavelengths appears, that does not

necessarily confirm the presence of that particular element. For example, the figure shows that the LIBS setup detects an extremely high signal of titanium. However, titanium has many numerous lines in the range of 200 - 800 nm and only two lines, one with an extremely low intensity, were detected. Titanium was detected in many concrete samples in many other similar studies as well, but the high intensity here does not reflect the quantity of this element in concrete [31,48–51]. Lastly, the signal of Na I was detected reliably and was in match with the corresponding salt concentration. In addition, the Na I and Cl I signals increased simultaneously, as expected. Yet, this LIBS setup appears to be more sensitive to the Cl I signal at lower salt concentrations ($< 0.7\%$). The increase in the contaminant dosage from 0.7% to 1.0% showed an increase in the Cl I signal as well, but it was not as noticeable as the change observed when the dosage was increased from 0.4% to 0.7%. The intensity of Na I, on the other hand, increased steadily even at high concentrations of sodium chloride.

After studying the signals of each key element in each test set, the signal of Cl I was further analyzed. Figure 27 and Figure 28 show the chloride intensity of each concrete sample. The X-axis shows the sample ID in the following format: Cement Type-Pozzolanic Additive-Chloride Concentration-Corrosion Degree. For instance, the code I-GGBFS-0.4%-8V corresponds to the Type I cement samples with GGBFS and 0.4% sodium chloride concentration that was subjected to 8 voltages from the PSU. From the graph, it is clear that the chloride intensity increases linearly with the increase in the amount of the contaminant. In addition, the addition of different pozzolanic materials did not affect the obtained signal. shows a similar plot for Type V samples. Similar trends were noticed for that sample set as well. The relations between the chloride concentration and the corrosion

rate are illustrated in Figure 20 and Figure 21. Figure 29 illustrates a sample for the variation of LIBS signal for one test set and Appendix B shows the spectra for all major elements.

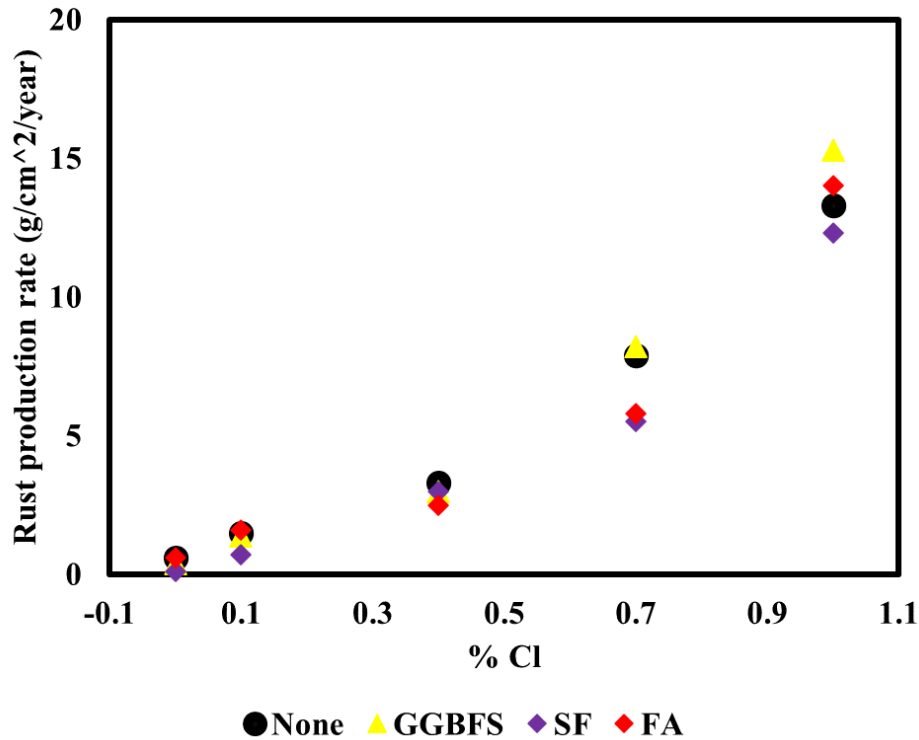


Figure 21 The effect of chloride concentration on rust formation rate for Type I samples

It is notable that the increase in Cl% significantly increased the corrosion rate. This is because chloride increases the resistivity of concrete and it contributes to the depassivation of the passive film on the rebar [9]. However, some studies suggest that high chloride concentrations reduce the corrosion rate because the chloride ions reduce the solubility of oxygen [17]. This is not clearly observed here and there are many other studies show that the corrosion rate keeps increasing with the increase in chloride concentrations even beyond 1.0%. The rust formation was observed even at 0% admixed chloride. This is attributed mainly to the induced current, but the mixing of water and the salt-based electrolyte can also contribute to this phenomenon. Although normal drinking water was

used, the chloride concentration in this water cannot be assumed to be exactly zero, especially with the fact that this water is most probably coming from desalination plants [18,19]. Deionized water could have been used, but this will reflect an inaccurate representation of the situation in Saudi Arabia where normal potable, desalinated seawater, is used for concrete mixing. Another factor contributing to the corrosion of the chloride-free samples is that the same concrete mixer was used to mix all the samples. Although the mixer was thoroughly cleaned after each use, a small amount of salt could have been left behind. These are still minor factors, as mentioned earlier, and the corrosion in the 0% Cl samples is mainly taking place due to the high applied current. The same pattern is observed in Type V samples but to a greater extent. That is, the corrosion rate was greater, which is expected due to the relatively lower chloride binding ability of Type V cement. A comparison between the rust production rate of Type I samples and Type V samples is shown in Figure 20 and Figure 21 respectively.

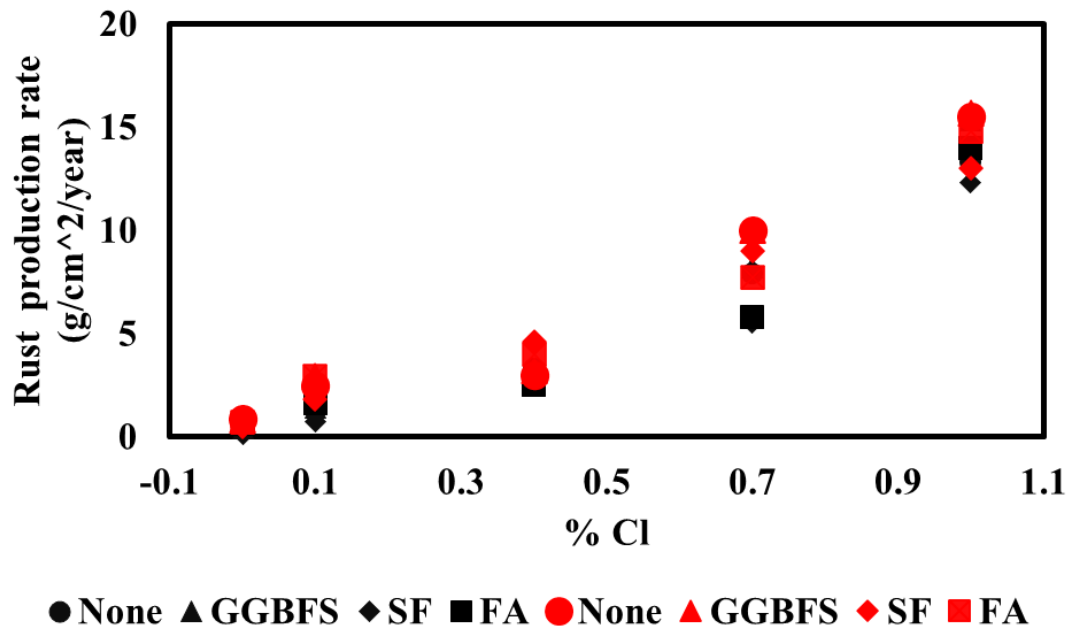


Figure 22 A comparison between Type I and Type V cement with respect to the corrosion rate

There is not much difference between blended cement and plain OPC at lower chloride concentrations ($\leq 0.4\%$). This is because this value appears to be lower than the critical chloride threshold, which is the point where rapid depassivation occurs and the effect of chloride binding becomes more significant [9]. In this particular sample set, that value seems to be slightly lower than 0.6% . at higher chloride dosages, the samples with different admixtures showed different behaviors. For example, at 0.7% , plain concrete as well as GGBFS-modified concrete showed a high rust formation rate while SF and FA samples maintained a lower corrosion rate. A somewhat similar trend can be seen with the 1.0% Cl samples where the GGBFS samples showed the highest rust production rate. The low resistance of GGBFS specimens can be ascribed to the extremely high dosage of GGBFS (50%), which contributes to the reduction of C3A. The change in the microstructure of concrete due to the addition of GGBFS in high quantities might have been an additional indirect factor contributing to the high corrosion rate. The high dosage of GGBFS can result in insufficient CSH content due to the lack of CH provided by the primary hydration reaction [20,21]. As a result, a weaker and less compact microstructure is formed that allows more electrolyte material (sodium chloride) from the corrosion setup to penetrate and cause even greater damage to the rebar. This effect is even more visible in higher chloride concentrations where the quantity of the produced iron oxide, which has a larger volume than iron and hence introduces radial stresses inside the concert, is high.

In contrast, SF concrete showed the best results in both Type I and Type V cement. The rust production rate was almost always minimal with the addition of SF. There are some occurrences where SF samples showed a higher corrosion rate, like in the 0.4% Cl samples in Type V cement, but at that point, the chloride binding effect appears to be less

significant, as discussed earlier. Thus, the corrosion rate cannot be solely explained by the effect of pozzolanic materials in that region. However, the next point on the same graph showed a similar trend where the corrosion rate of the SF samples was not the lowest, but the second lowest. The most obvious trend with respect to SF samples in both graphs, nonetheless, is that they always result in better corrosion resistance performance in this particular test environment. This trend is more apparent at the higher chloride concentrations where the other additives caused a noticeable increase in the corrosion production rate. The effect of silica fume can be explained from three aspects. The first of which, is the low amount of silica fume (7%), which means that the binder is still almost entirely pure cement and hence contains a high amount of C3A. The second reason behind the low corrosion of the SF-modified samples is the excellent filling ability of the extremely-fine SF particles; giving a much denser microstructure to the concrete [4,22]. Finally, SF increases the resistivity of concrete and thus delays the corrosion reaction [23].

The average rust formation rate for each Type V sample was calculated and the relation between the rust production rate (denoted as J_r) and the chloride concentration was developed. Figure 23 graphically represents this relation and shows vertical error bars to indicate the calculated standard deviation. Figure 24 shows the same relation for type I samples. The coefficient of determination shows the degree of correlation between the presented model and the average corrosion rate from each sample set. Table 7 shows similar models where the corrosion current density, which can be derived from the rust formation rate (J_r), is related to the chloride concentration and some other factors. In Ahmad and Bhattacharjee mode, the letter C represents the chloride concentration and it can be seen in two terms; similar to the presented model. Jung's model, however, used

exponential fit. In this experiment, however, the exponential fit yielded less accurate results, as shown in Figure 25 and Figure 26.

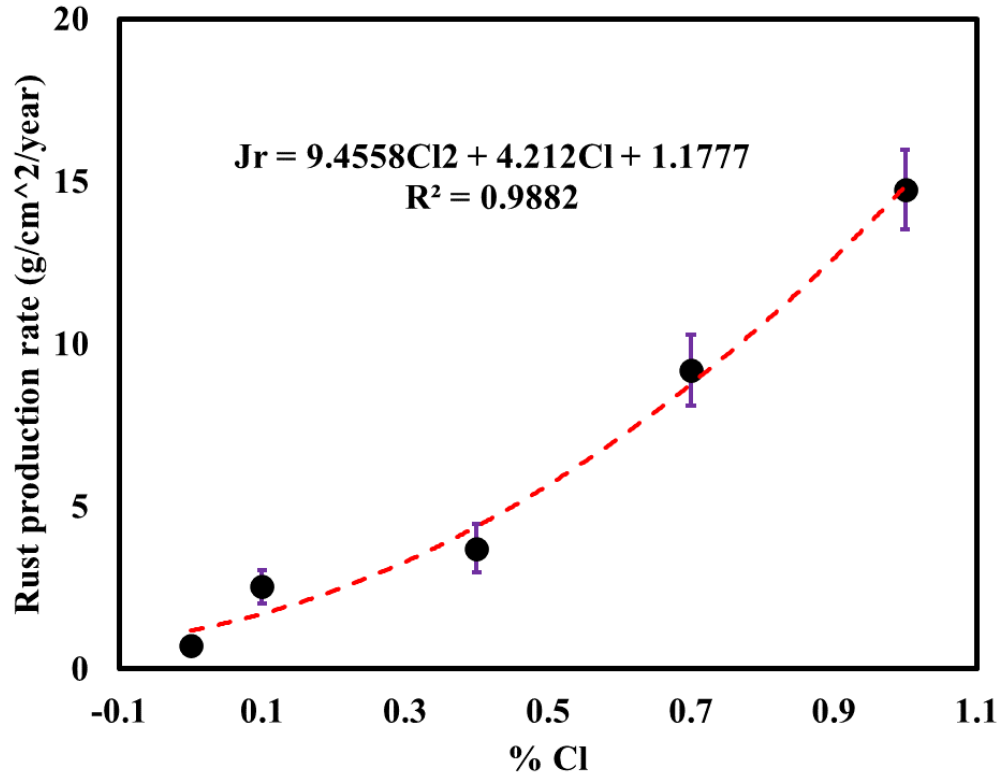


Figure 23 The developed quadratic model for Type V samples

The first set in Figure 29 at 0% admixed chloride concentration still shows a low signal, this can be also seen in similar studies [52]. This might be due to the remaining residues of chloride in the concrete mixer, although it was thoroughly cleaned after each mixing set, a small amount of remnant materials is unavoidable. In addition, chloride could have been present in the mixing water, although normal drinking water was used. This claim is supported by the fact that most of the drinking water in the Eastern Region of Saudi Arabia, where this research was conducted, is desalinated seawater [53,54]. The signal, nonetheless, was extremely low and the increase in chloride concentration from 0% to 0.1% was very clear. The intensity linearly increased after that to a max of about 6000 at 1.0%

Cl content, more than six times the figure observed at 0% concentration. This linear relation was observed in similar studies [55,56]. The relation is presented for both types of cements numerically in Table 6 along with the value of the coefficient of determination. The min value of R^2 was 0.96 which indicates a high level of correlation. There was a slight variation between the readings obtained from the samples with Type I cement and from the samples where Type V cement has been used. However, the main trend shown in both cases is that the intensity of the LIBS signal appears to be linearly related to the concentration of Cl.

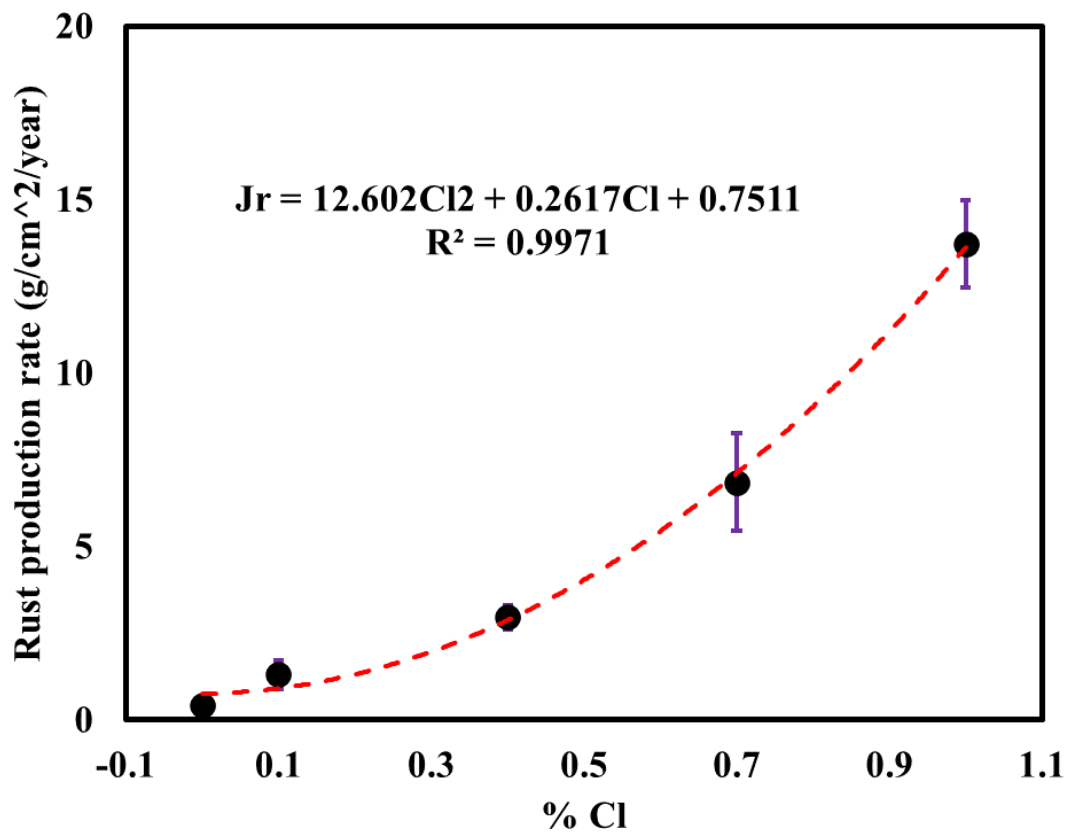


Figure 24 The developed quadratic model for Type I samples

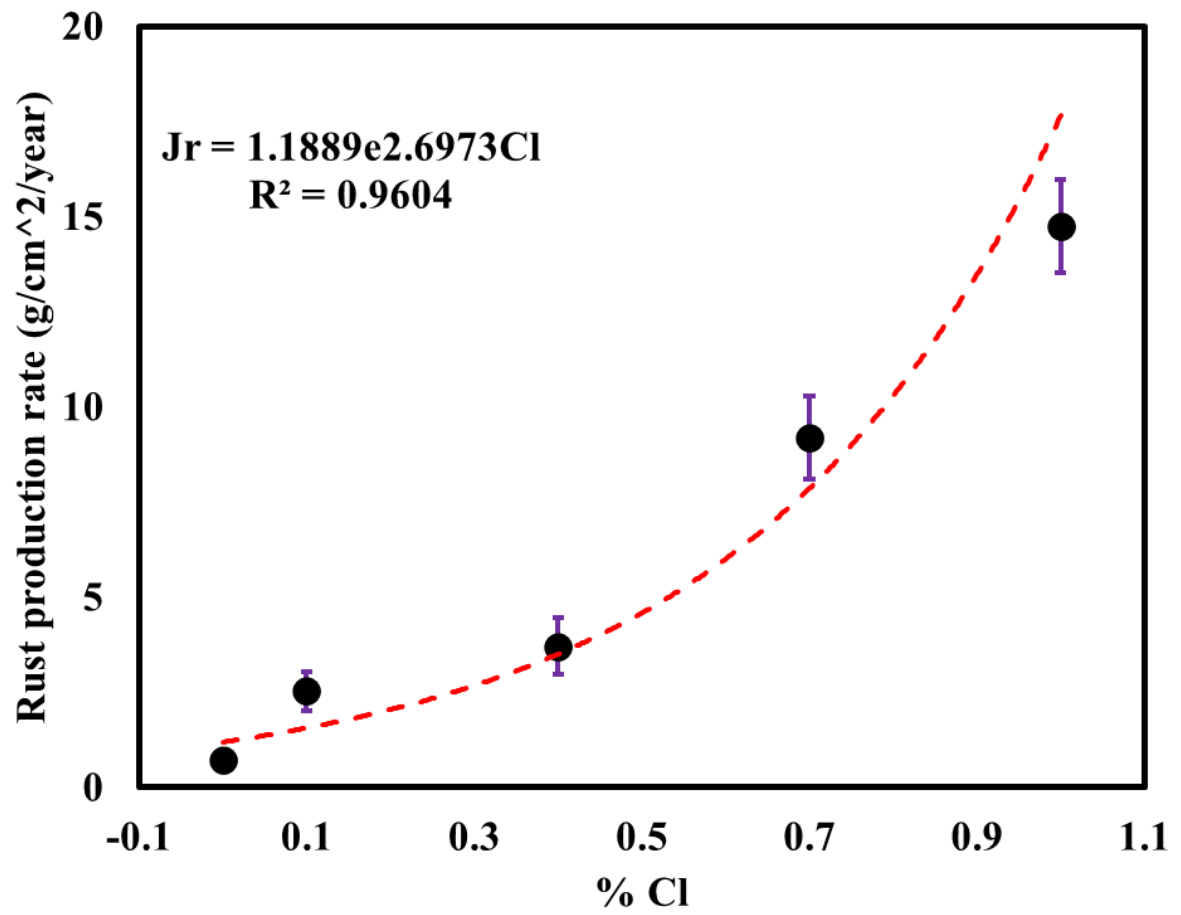


Figure 25 The developed exponential model for Type V samples

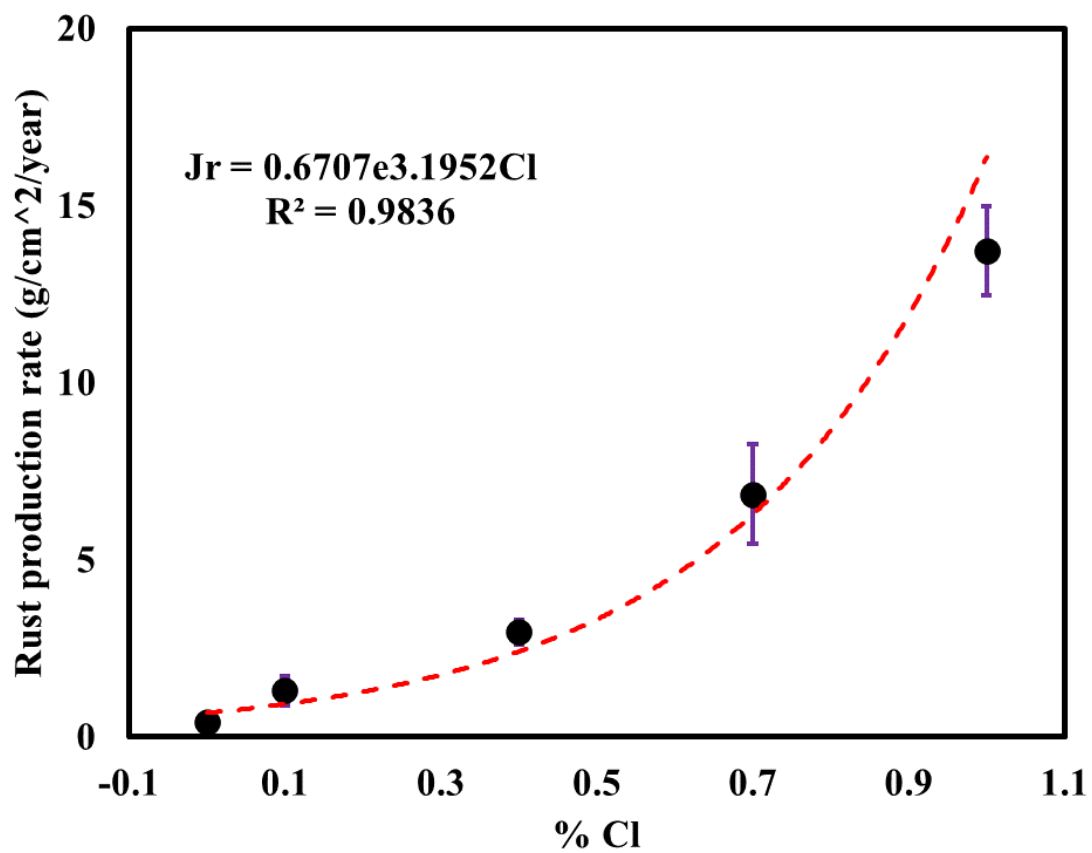


Figure 26 The developed exponential model for Type I samples

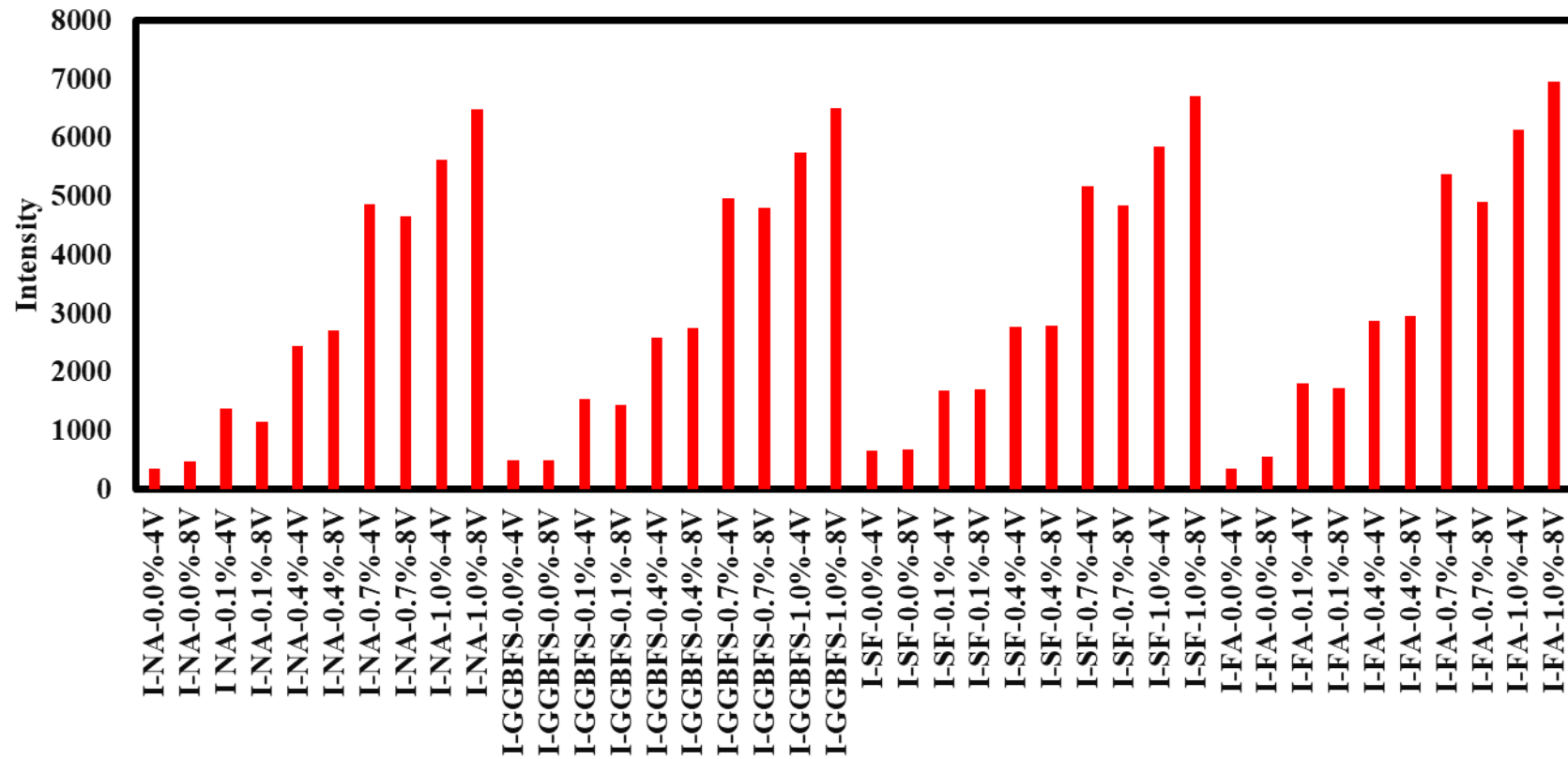


Figure 27 Chloride intensity in each Type I sample

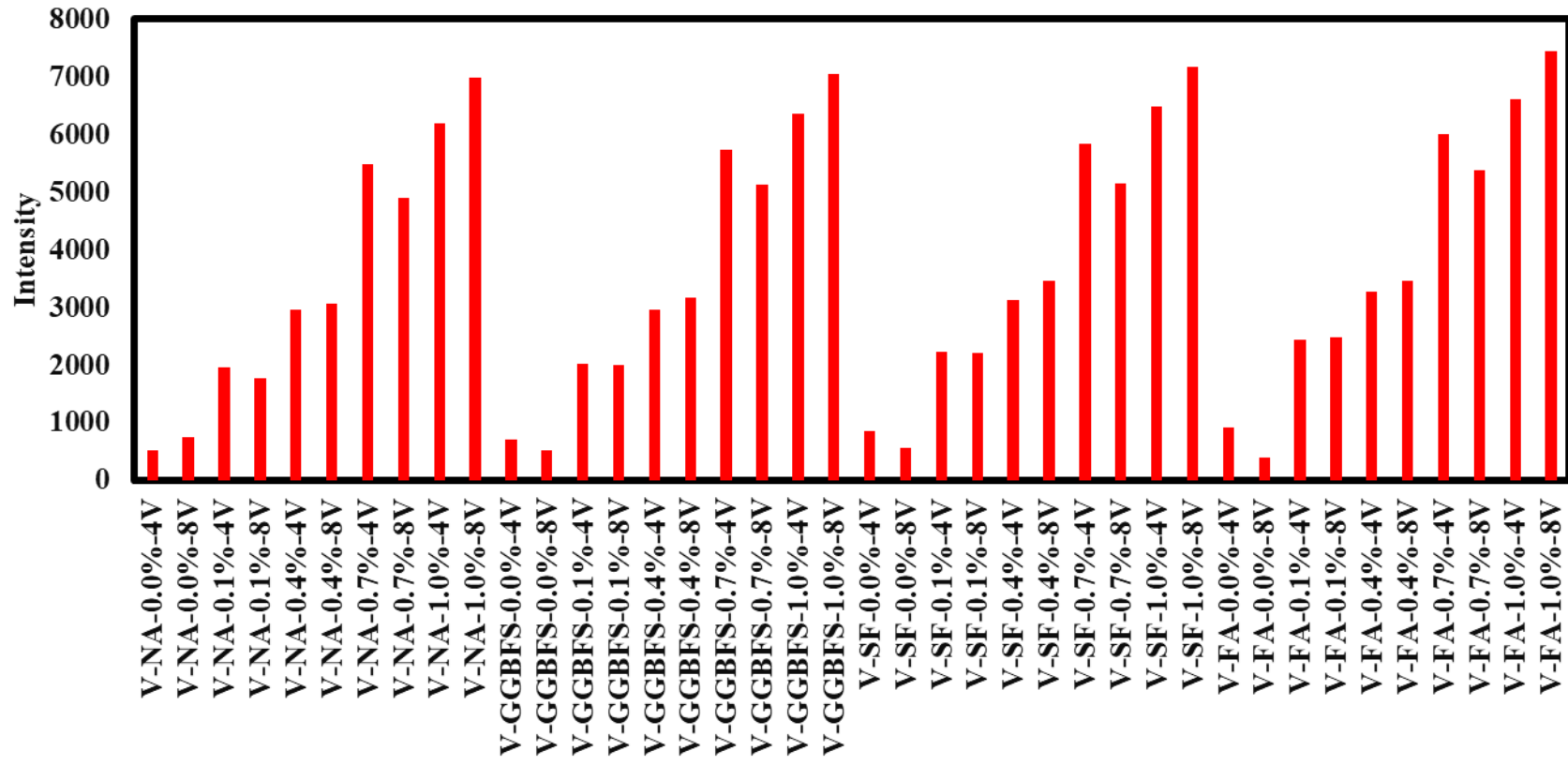


Figure 28 Chloride intensity in each Type V sample

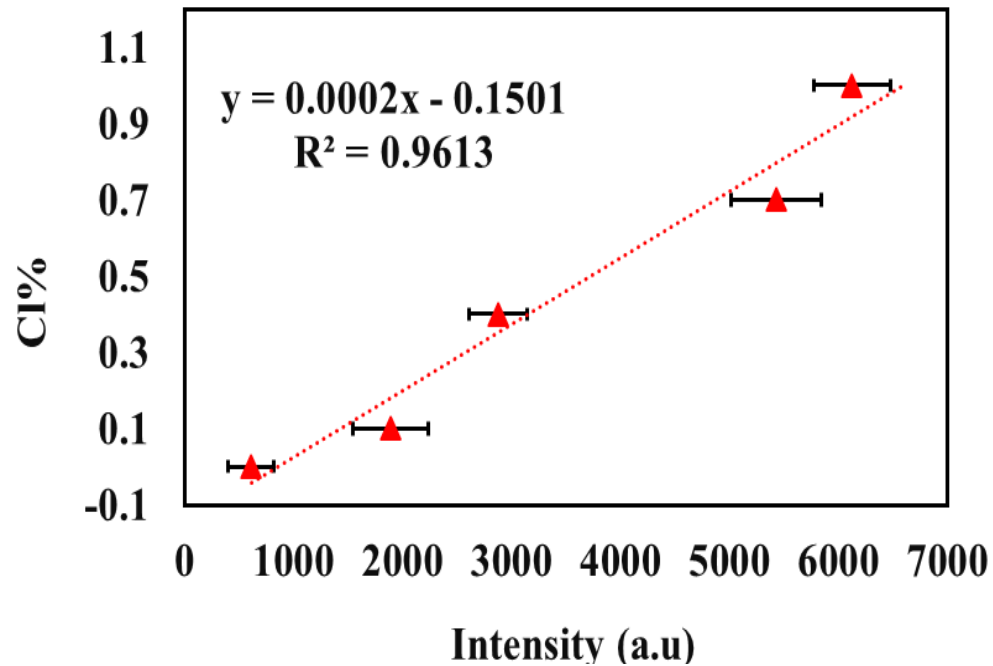


Figure 29 The variation in signal between all the tested samples along with the governing relation

While it is true that an empirical model could be developed to determine the chloride concentration in concrete by utilizing the diffusion coefficient, such a model will only be valid in the same testing environment. For instance, if an empirical model is to determine the chloride concentration in concrete samples with a 0.45 w/c ratio, it cannot be assumed that the same model will work for concrete samples with a 0.3 w/c ratio. This is because the microstructure of concrete affects the penetration rate of chloride. In addition, such models require extra input, such as the cement type and the cement quantity, which are not always available. This point is particularly important if the structure to be investigated was already built and there is no documentation for the composition of the concrete used to build it. The presented model to measure the chloride concentration in concrete addresses this point. The model shows that the used setup was able to detect chloride in concrete samples with different compositions (different cement types and different additives) while maintaining the same output. In other words, the presented LIBS setup was able to

accurately measure the chloride concentration in concrete regardless of its composition. Moreover, the proposed LIBS model has a high R^2 value, which is difficult to maintain when analyzing concrete due to its heterogeneity. However, the usage of LIBS, although it is a point analysis method, still manages to take care of this issue by shooting multiple spots of the material under analysis. This is equivalent to increasing the sample size and thus gives a better representation of the targeted analyte and, consequently, produces better results, which also explains the high R^2 value. This can surely be done with any other method, but LIBS laser takes a few milliseconds to complete the process of ablation and sending the signal to the PC, which displays the results instantaneously. The process of analyzing many spots from one sample takes time with other conventional testing methods.

The %loss in weight of rebar should not be correlated only to the chloride concentration because corrosion takes place with time as well. Thus, the byproduct formation rate was calculated and then correlated to the Cl concentration under the given conditions. Figure 20 and Figure 21 also show the results of the weight loss analysis where the horizontal axis gives the chloride concentration and the vertical axis represents the rust formation rate. The figure shows that the samples with 0% admixed chloride also suffered from corrosion, but it was minor. This is due to the effect of the current-induced corrosion. It is also noticeable that a small increase in the chloride content highly affects the corrosion process. The relation between the byproduct formation rate and the chloride concentration is shown in Table 7 along with their corresponding coefficients of determination. The min value of R^2 was 0.89, which confirms that these parameters are related. In addition, similar models to calculate the corrosion current density, which can be derived from the rust formation rate, are presented. The models confirm that the rust production rate is adversely affected by the

presence of chloride and this relation is not linear. Instead, the model is represented in an exponential or a quadratic equation, which reflects the high impact of chloride on the corrosion degree.

Table 6 The developed relation between the chloride intensity and LIBS signal

Relation	R²
Type I	
[Cl] = 0.0002 * intensity - 0.0951	0.97
[Cl] = 0.0002 * intensity - 0.1237	0.97
[Cl] = 0.0002 * intensity - 0.1551	0.96
[Cl] = 0.0002 * intensity - 0.1187	0.97
Type V	
[Cl] = 0.0002 * intensity - 0.0897	0.98
[Cl] = 0.0002 * intensity - 0.1321	0.96
[Cl] = 0.0002 * intensity - 0.0923	0.97
[Cl] = 0.0002 * intensity - 0.1003	0.97

Table 7 The developed relations between the chloride intensity and the rust formation rate (Jr)

Admixture	Jr (gm/cm2/year)	R ²
Type I		
None	$17.168[\text{Cl}]^2 - 1.7827[\text{Cl}] + 1.7363$	0.89
SF	$7.439[\text{Cl}]^2 + 4.7676[\text{Cl}] + 1.5902$	0.92
GGBFS	$13.832[\text{Cl}]^2 + 0.5729[\text{Cl}] + 1.1816$	0.90
FA	$13.53[\text{Cl}]^2 + 0.0525[\text{Cl}] + 1.6836$	0.97
Type V		
None	$16.989[\text{Cl}]^2 - 4.5027[\text{Cl}] + 0.7$	0.86
SF	$8.9056[\text{Cl}]^2 + 3.7653[\text{Cl}] + 0.6866$	0.93
GGBFS	$13.622[\text{Cl}]^2 + 0.91[\text{Cl}] + 0.7771$	0.98
FA	$10.932[\text{Cl}]^2 + 0.7344[\text{Cl}] + 0.3673$	0.91
Similar models		
Ref.	Model	
[57]	$I_{\text{corr}} = 37.726 + 6.120 C - 2.231 A^2 * B + 2.722 B^2 * C^2$	
[58]	$I_{\text{corr}} = 0.0692 \exp [1.69848 * \text{Cl}]$	

CHAPTER 4

Conclusions and Recommendations

1.1 Conclusions

This research showed the potential usage of LIBS as a tool to estimate corrosion rate and its outcomes could be useful for developing a standard methodology in which concrete is tested using LIBS. It presented a relation between the corrosion degree and the chloride concentration from LIBS analysis. On one hand, our LIBS device showed that there are 14 dominant peaks in the range between 200 - 800 nm. Some of these lines showed a reliable signal and can be used in future studies to analyses concrete. For example, Cl I at 574.9 and Na I at 616.1 can be used to detect chloride. The setup was also able to detect minor changes in Cl concentration and that was reflect accurately on the output signal. In addition, linear relations between the LIBS signal and the chloride concentration were obtained with high R^2 value. On the other hand, weight loss due to the current-induced corrosion setup was also correlated to the chloride concentration. The presented LIBS relations in Table 5 can be used to determine the chloride concentrations in a given concrete sample then the relation between the chloride concentration and the rust formation rate can be used to determine the corrosion degree. The results were compared with other previous studies and they were in con-format.

1.2 Recommendations and suggestions for future studies

Besides the outcomes that was presented in the previous section, we would like to present some recommendations to ease the prospective work on this field by providing the following suggestions:

- The removal of resistors from the corrosion board might be considered if high voltage is to be applied to avoid fires.
- Wider laser spot can be used to scan larger areas of the sample and to obtain a more representative shot.
- The laser type, inter-pulse delay, laser energy, and other specifications should be in accordance with the literature to generate more data at a given input. This will help create a more accurate model and enable the utilization of AI to develop more precise models.
- The laser amplification of the lab device should be taken into account when applying the same experiment on a handheld device.
- The corroded samples should be well-confined with counter electrodes to ensure the electrolytic concentration.

LIBS technique is becoming more and more popular every day yet, there are still some blanks for development to fill in the field of LIBS technology. This project revealed some of the areas that could be improved when it comes to the detection of contaminants and rust on rebar and concrete samples; these are listed below:

- Overcoming the high calcium absorption rate,

- Mathematically minimizing the matrix effect by means of computer algorithms by utilizing the fixed cement composition,
- Assessing the ability of LIBS to analyze rebar instead of concrete contaminants,
- Optimizing a LIBS setup that aimed solely to analyze concrete, which is beneficial due to the extensive use of concrete, and
- Assessing the applicability of the presented model on other types of concrete, including ultra-high-performance concrete and self-compacting concrete.

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Appendix A

Summary of the reviewed papers

Application	Setup	Sample type	Most significant lines/elements detected	Remarks	Ref.
Analyzing hardened concrete to determine the type of cement.	Diode-pumped low-energy laser (1064 nm, 3 mJ, 1.5 ns, 100 Hz) with UV and NIR spectrometers	1 – Dried and pressed pellets 2 – Dried only 3 – Untreated	Si I, Al I, Fe II, Ti II, Ca II, Mg I, Na I, K I, Na I, K I, S I, OI	The study demonstrates that LIBS can be used to identify various types of cement. The study also suggests that other properties of concrete, such as the aggregate type and content, might be assessed using LIBS as well.	[154]

Determining the concentration of hazardous materials in a concrete dam.	Q-switched Nd:YAG laser (Brilliant-B Quantel, France; able to deliver 450 mJ at 532 nm), 10 Hz repetition rate, 2 μ s delay, 5 ns pulse width, and a 10 cm lens to focus the laser beam with laser energy from 200 to 400 mJ.	Pellets pressed under 30 tons for 30 minutes.	Mn and Si at 285.21 nm and 288.16 nm. Ca I at 526.17 nm, 526.56 nm, and 527.02 nm. Ti I at 519.29 nm and 521.04 nm. Ca, K, Fe, Al, Sr, and Li were detected as well.	LIBS results were compared with LA-TOF-MS results and were found similar. [158]
Using LIBS to develop an AI-based technique to differentiate between coarse aggregate and mortar in hardened concrete was developed.	Diode-pumped Nd:YAG laser with (1064 nm, 100 Hz, 3 mJ) supplied by Secopta fiberlibslab with 525–750 nm NIR and 745–940 nm VIS spectrometers	1 – Aggregate with epoxy resin 2 – Cement with deionized water 3 – Conventional concrete. All untreated.	H, C, O, Ca	The study claims almost 100% accuracy. [144]
Analyzing powdered cement.	1064 nm Q-switched Nd:YAG laser; 1 Hz, 10 ns, 37 mJ	12 mm x 1 mm pellets pressed under 12 mpa for 5 min	Ca I, Si I, K I, Mg II, Al I, Na I, Ti II, Mn II, Sr II	The LOD and the optimum delay time for various constituents were also presented. [201]

Online quality control in a cement plant.	1064 nm Q-switched Nd: YAG laser, 80 mJ pulse energy, 8 ns pulse width, and 20 Hz pulse repetition rate, and focal spot diameter of approximately 200 µm. Single-channel spectrometer (avaspec-2048FT-USB2, 230–450 nm, 0.1 nm spectral resolution)	Gas-powder mixture directly from the cement conveyor pipe	Ca II, Ca I, Si I, Fe II, Al I, Mg II	Details about the ideal powder concentration and the laser power were presented.	[197]
Detection of chloride in concrete.	Two Q-switch pulsed Nd:YAG lasers (Sky lasers) of which a fourth harmonic (266 nm) laser and a fundamental (1064 nm) laser were aligned so that the two laser spots fall on the same spot	Pellets	Cl I at 837.5 nm and 594.8 nm	The system was able to detect the presence of chloride up to 0.2%, which is the maximum allowed limit of chloride in RC by some design codes.	[43]
Detection of sulfur in concrete.	1064 nm, 10 ns, 300 mJ/pulse Nd:YAG laser (Big Sky) shooting at a lens with	1 – 5 cm cement pellets	Sulfur spectral line at 921.3 nm	Sulfate was successfully detected in concrete cores and the experiment. The paper also emphasized	[193]

	500 mm focal length and a spectrograph (pectrapro-150) and a CCD. Measurements accomplished under air, argon and helium atmosphere	2 – 5 x 5 x 15 cm cement prisms 3 – 5 x 5 x 15 cm mortar prisms 4 – 15 x 15 x 15 cm concrete prisms		LIBS' enhanced depth and spatial resolution.
Detection of chloride in cement paste.	(optimum setup reported): dual-pulsed system with 4 L/min helium gas flow rate, 2000 ns pulse delay, 800 ns gate delay, 19 mJ/ 11 mJ pulse energy ratio, and 42.8 mm lens-to-sample distance.	Cement cylinders broken and ground to 75 µm particles then pressed under 250 mpa to form cement sheets.	Chlorine at 837.6 nm	SNR was improved from 1.75 to 2.68 using microwaves. According to the study, the LOD was 47 ppm. [170]
Detection of chloride cement paste.	Dual-pulsed, single pulsed, and LIBS-LIF lasers were all used. Spot dia. Varied from 60 – 400 nm, delay time varied from 0.5 – 50 µs, and 266, 1064,	Dried pellets. Pressed under 100 mpa for two minutes.	Cl at band 837.6	12 labs, each with their own testing method, from various countries attempted to detected chloride in cement samples with concentrations ranging between 0.06% and [169]

	and 532 nm lasers were used.			1.95%. The margin of error was found to be less than 15%.	
Microwave-assisted LIBS for chlorine detection in concrete	A Qswitch Nd:YAG MW-LIBS with a repetition of 10 Hz was used. A fused silica lens with 100 mm focal length was used to focus the laser into a 140 mm ² spot. Also, a 3.5 – 10 mJ laser energy was considered.	Dried pellets.	Cacl at 593.5 nm, 606.4 nm, 617.9 nm and 620.5 nm.	SNR of chlorine at 837.6 nm was 2.68 for a sample containing 0.706 wt% chlorine	[22]
Detection of chloride in mortar.	532 nm Nd:YAG laser of 320 mJ, in a helium atmosphere	40 x 40 x 160 mm prisms were prepared following the EN 196-1:2005 standard then they were cut to smaller pieces to perform different kinds of tests. The LIBS spaceman size was 20 x 20 x 20 mm.	Cl I 837.60 nm and Ca II 849.80 nm	The samples were subjected to seawater for 5 years. The results were compared with standard chloride detection methods. As per the study, LIBS was an accurate and effective method to detect chloride.	[23]

Determination of the chloride diffusion coefficient in mortar and concrete.	A 532 nm Nd:YAG laser of 320 mJ (generating radiation pulses 10 ns long at a 10 Hz) in a helium chamber.	40 x 40 x 40 mm prisms.	Cl I at 837.60 nm	The samples were subjected to chloride for up to 5 years and the measured results agreed with the typical diffusion coefficients from other studies.	[44]
Evaluating the effectiveness of embedded zinc anodes to extract chloride ions in concrete.	Passive Q-switch ndcr:YAG-laser: 1064 nm, 3 mJ, 1.5 ns, 100 Hz combined with a NIR (750 nm - 950 nm) and a UV (230 nm - 500 nm) spectrometers.	85 mm by 65 mm galvanic anode/mortar probes which were fine-cutted.	Ca, O, K, Na, Cl, C, S, Ca, Si, Mg, Al, Fe, Ag, Ti	LIBS results were logical; the embedded anode worked as expected and the level of chloride was sufficiently reduced.	[152]
Analyzing blended cement pastes.	Diode pumped ndcr:YAG laser (1064 nm) with a pulse energy of 3 mJ, a pulse repetition rate of 100 Hz, and a pulse length of 1.5 ns was used (fiberlibslab Secopta analytics gmbh). The spot size was approximately 80 µm.	Tablets of 40 mm diameter pressed with approximately 100 mpa.	Cl I at 837.6 nm	The chloride concentration in 55 samples, and 7 different mixtures, was determined using LIBS and titration. As per the study, the difference between the results was 0.05 wt%.	[42]

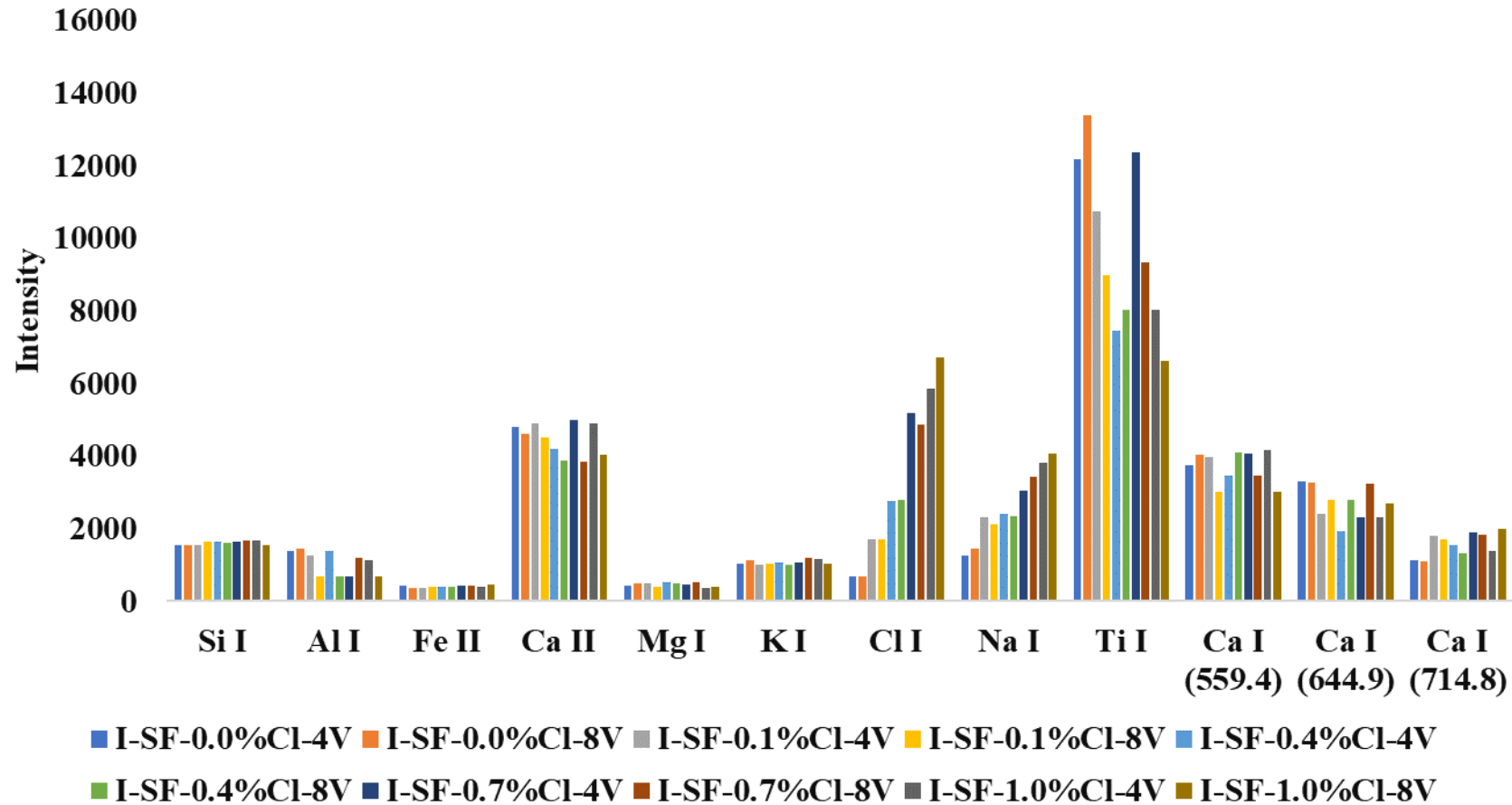
	Two spectrometers and a charged coupled device camera running in 175 nm to 360 nm in the UV range and 740 nm to 940 nm in the NIR range.				
Determining the sulfate concentration in concrete samples.	Dual-pulsed 1064 nm fundamental and 266 nm fourth harmonic Nd:YAG laser in conjunction with Spectrograph/gated ICCD from Sky Lasers	25 x 25 x 8 mm pellets	S II peak at 545.38 nm	The limit of detection was determined to be 38 µg/g.	[24]
Sulfur detection in concrete.	532 nm in a He chamber. 100 mJ, 5 pulses per spot.	Pellets	Sulfur at different lines.	Different lines of sulfur were detected and different experimental setups were tested. The samples contained 0.43 – 0.61%. LIBS measurement was 0.41 – 0.70%.	[190]
Sulfate ingress profiling.	Ndyag-Laser (Big Sky), a monochromator (Acton Research spectrapro 150 with	Concrete cores of 100 mm diameter	Sulfur spectral line at 921.3 nm	A continues sulfate profile was generated using LIBS an compared with the one	[45]

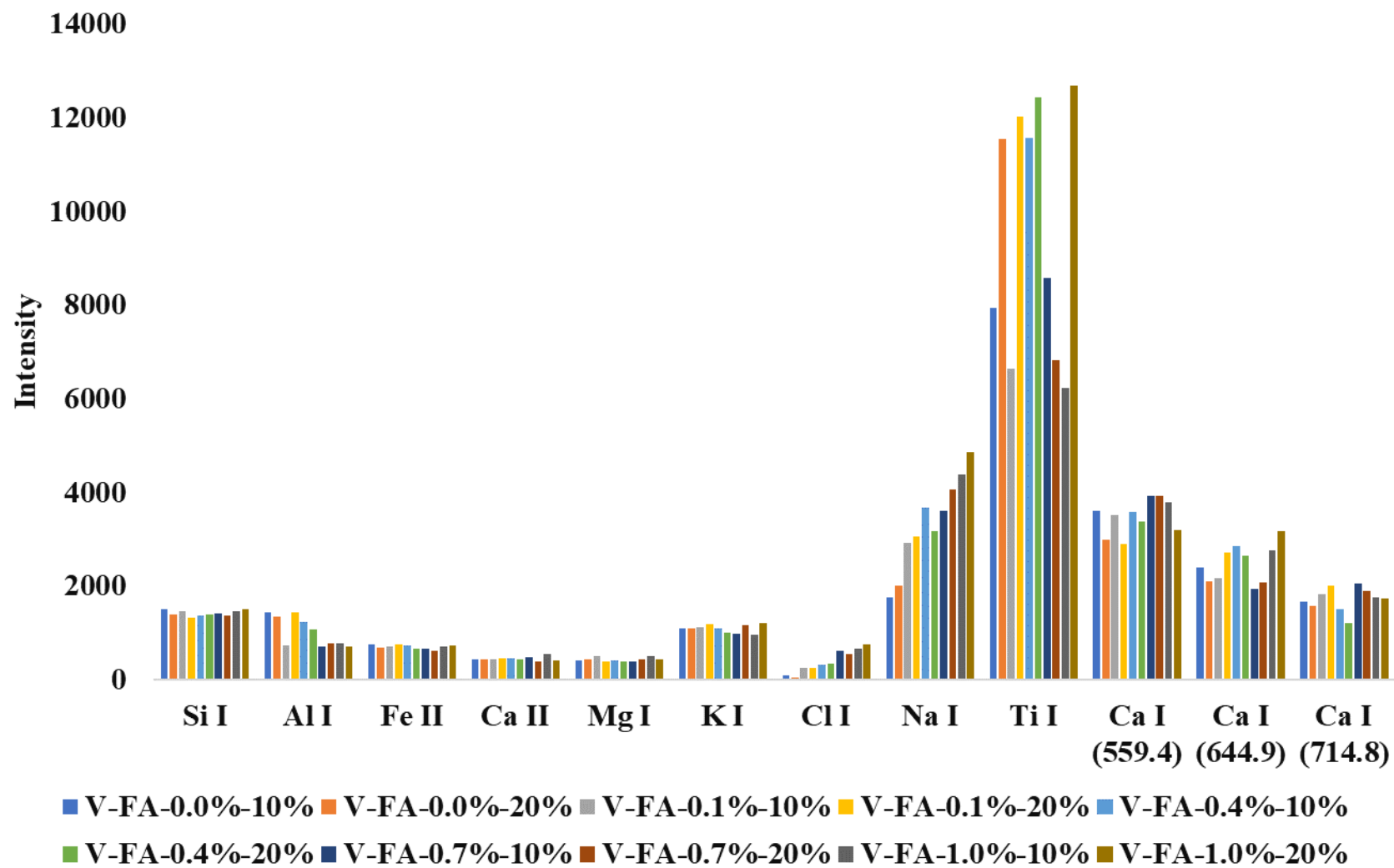
	1200 L/mm grating), and a CCD-cameras (OMA 4, EG&G, and Andor DV 420- OE). Laser wavelength was 1064 nm, laser power of 300 mJ/pulse, 10 Hz frequency, exposure time of 51 ms for each laser shot, and a 5 l/min He flow rate	which were sliced in half.		obtained from a typical analysis method.	
Detection of rust products in concrete.	Second-harmonic radiation from a Nd:YAG laser with a LOTIS LS-2134UTF pump (532 nm, pulse energy 80 ± 1 mJ, length of 6 ns, and frequency of 5 Hz) was used at a focal length of 150 mm. A portable device (LIBS Z-200 from sciaps, USA) was also used.	200 × 60 × 60 mm reinforced concrete blocks with Ø10 bars	Fe, Mn, Cr	Iron, manganese, and chromium were detected using a handheld LIBS device on the concrete surface. However, the signals were only reliable on the areas covered with rust stains.	[194]

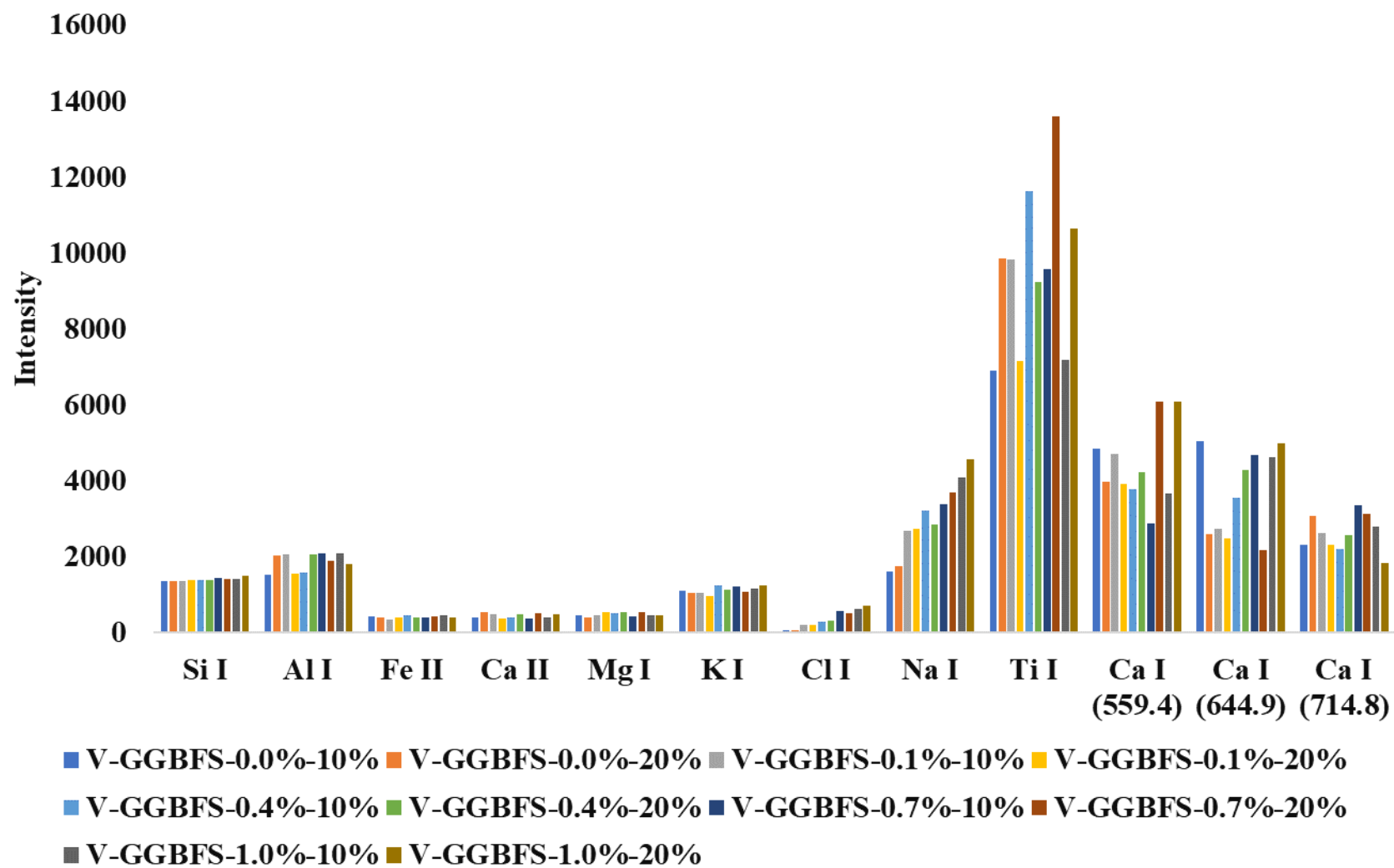
Ion mapping in concrete overlays	Fiberlibslab device from SECOPTA (1064 nm, 3 mJ, 1.5 ns, 100 Hz, passive Q-switch, ndcr:YAG-laser) . Laser spot is 80 µm in diameter. NIR 750 nm - 950 nm and UV 230 nm - 500 nm spectrometers were used.	Sliced concrete cylinders. The scanned area was 85 mm by 65 mm.	Ca, Si, Mg, Al, Fe, Ag, Ti, O, K, Na, Cl, C, S	It was possible to analyses the concrete matrix and represent the ions distribution that is caused by the electrical field visually.	[179]
Sensitivity enhancement of 594.8 nm Cl I detection in reinforced concrete	10 Hz, 9 ns 120 mJ ,1064 nm Q-switch pulsed Nd: YAG laser (Quantel Brilliant B) and a focusing lens of 70 mm focal length	Pallets	Chlorine at 594.8 nm and 837.5 nm	A weak line of chlorine was studied for quantifying chloride in concrete samples. The line of chlorine at 594.8 nm showed a high sensitivity despite its weak intensity due, indicating that this line suffers a less quenching and reabsorption compared to the line at 837.5 nm in a concrete matrix.	[40]

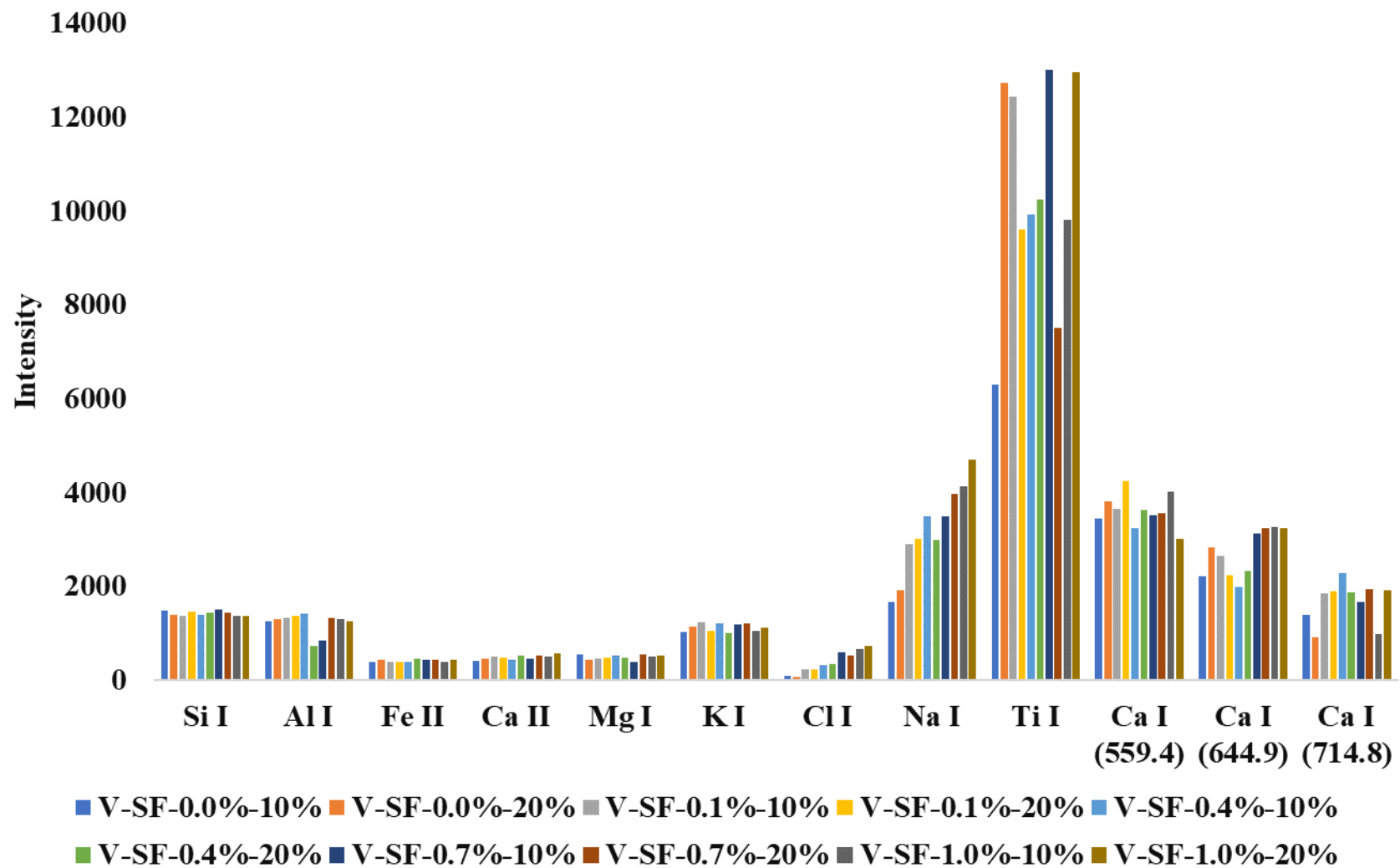
Appendix B

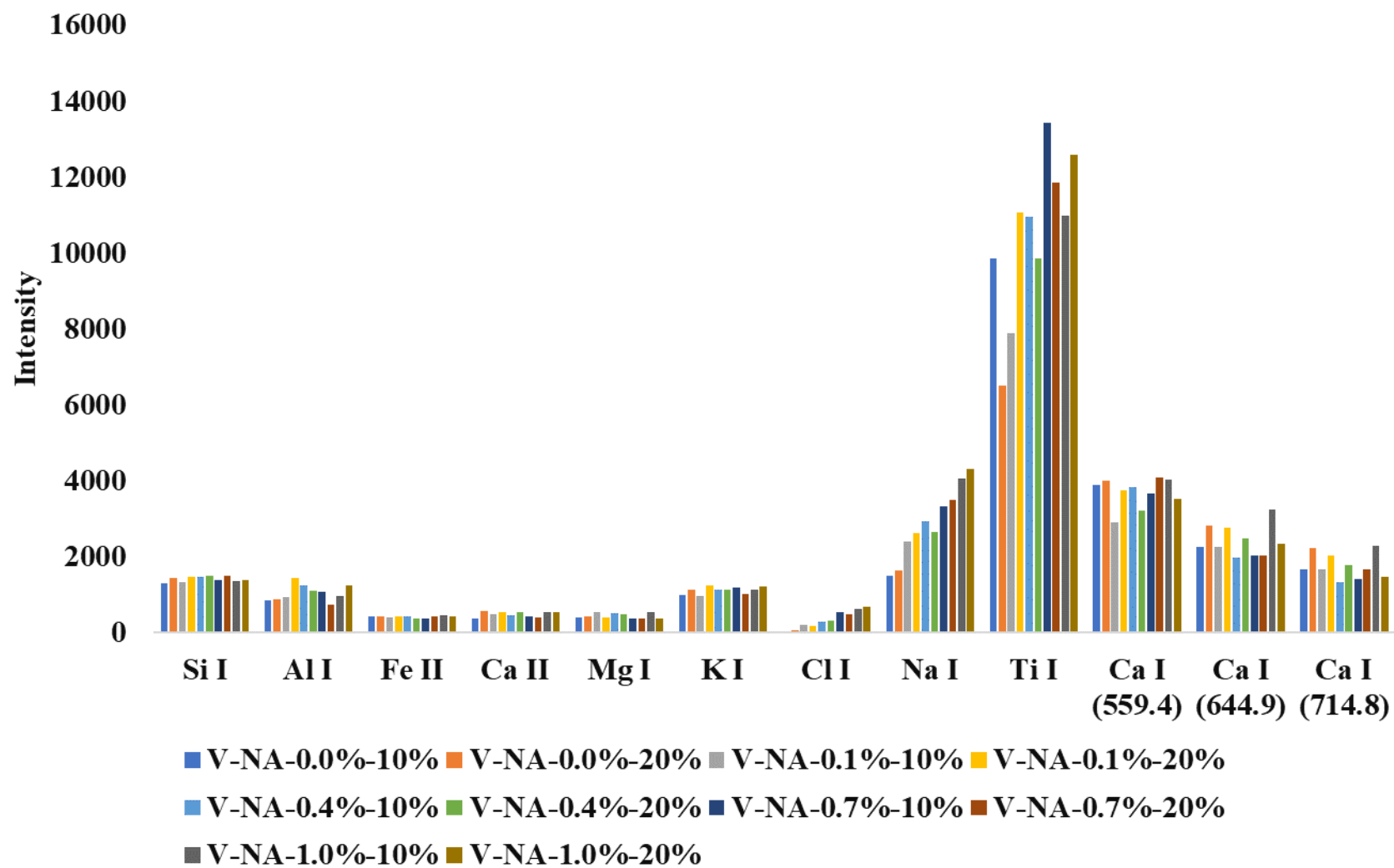
Spectra of major elements

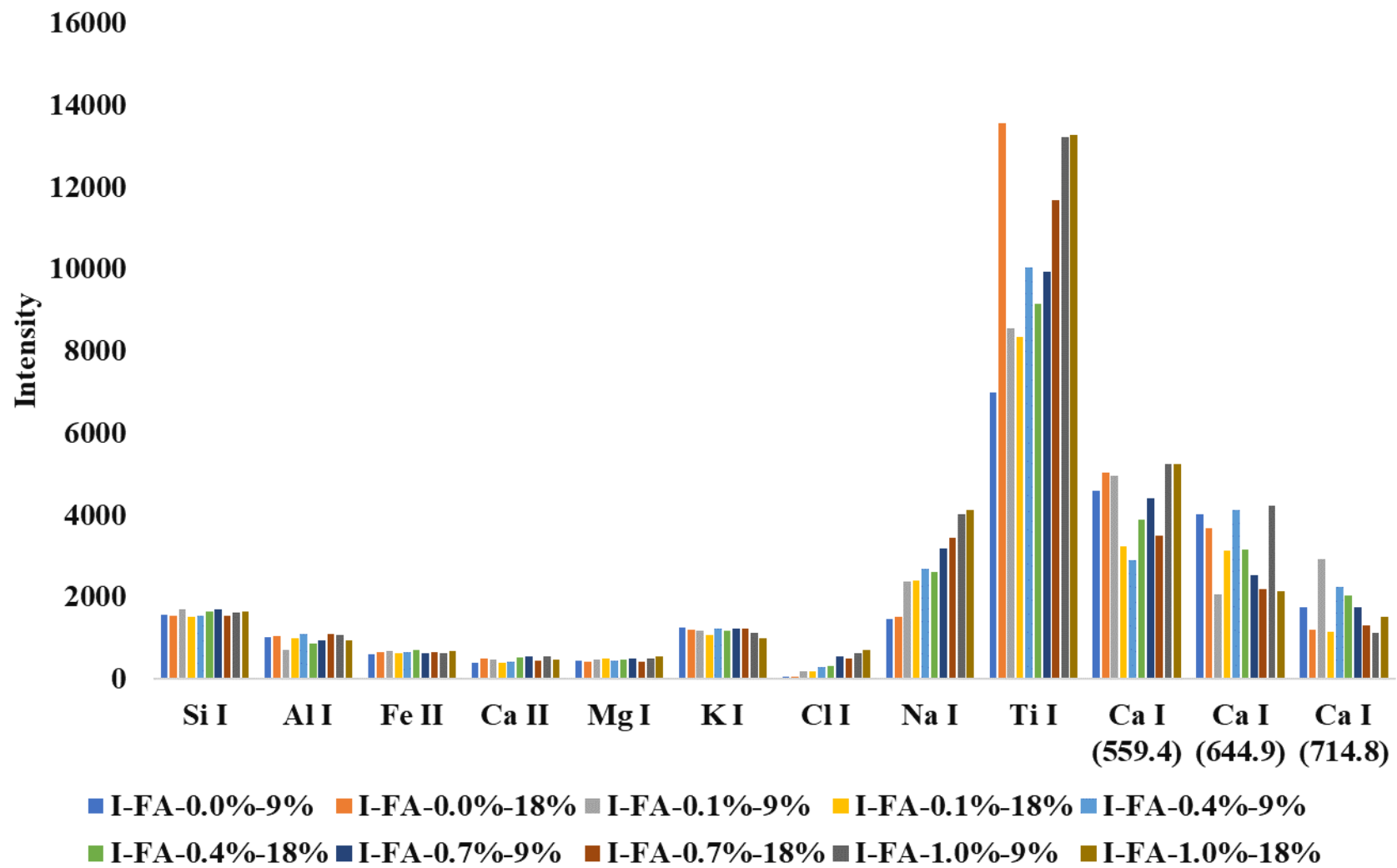


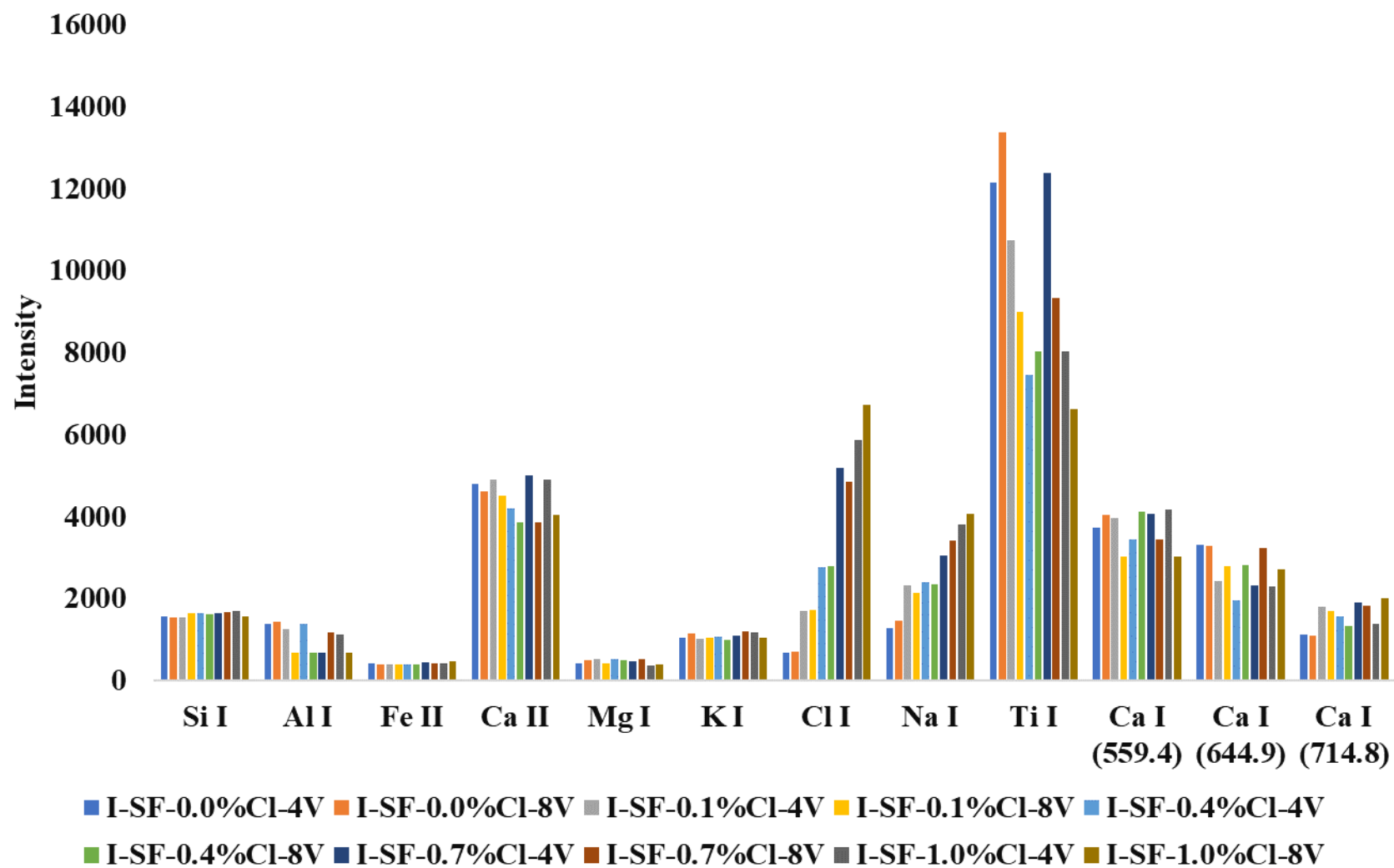


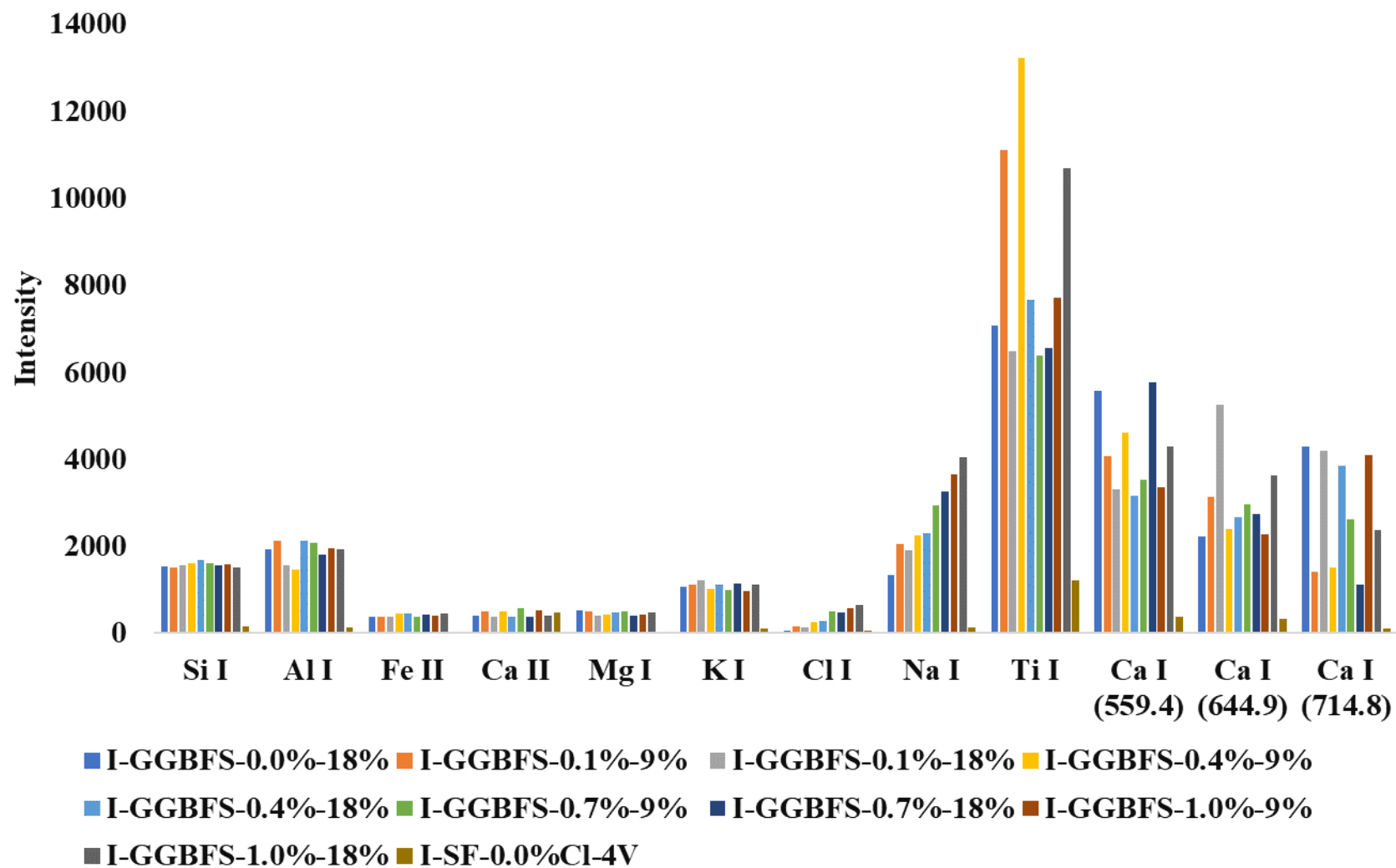


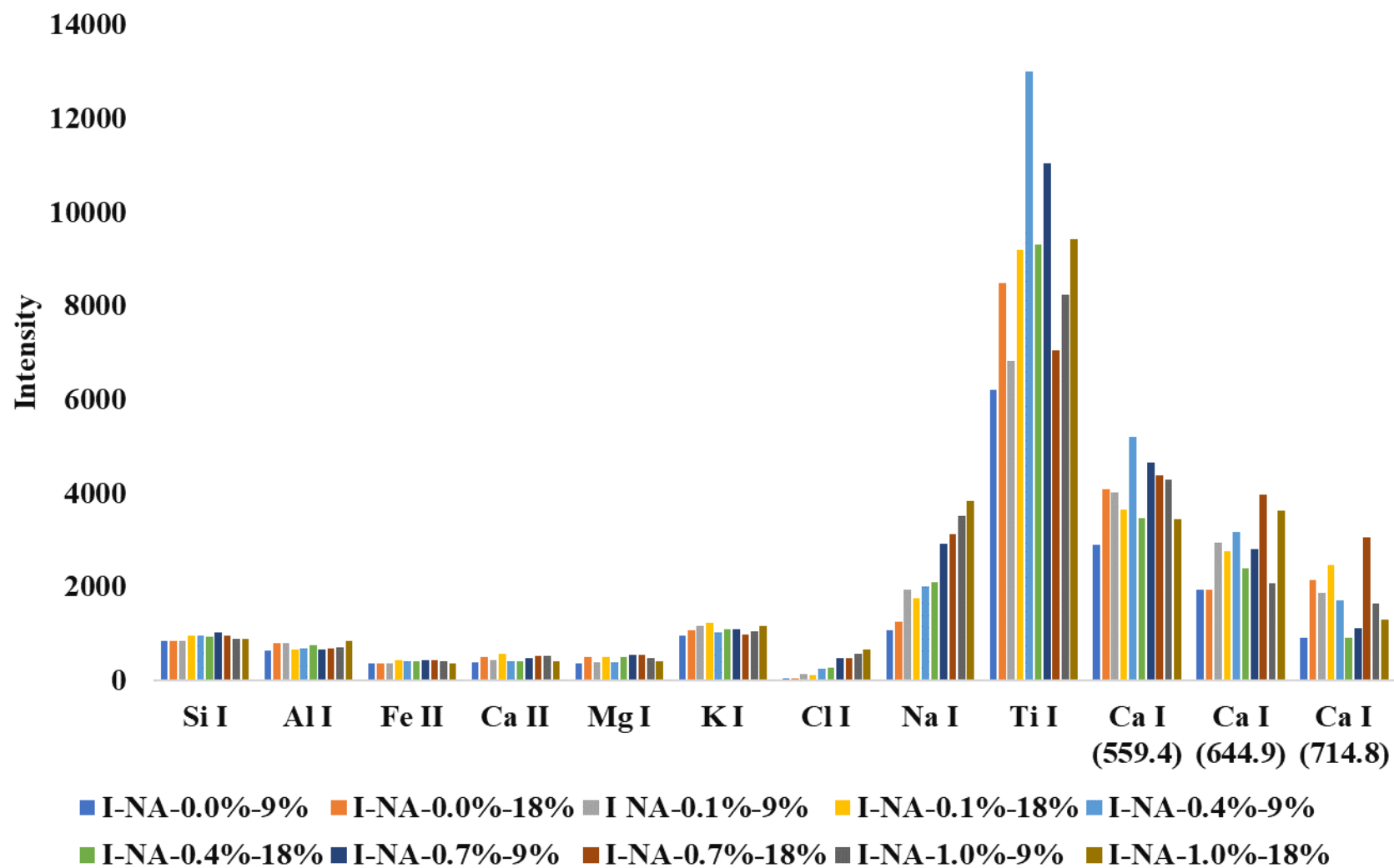












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