MICROSTRUCTURAL DEVELOPMENT AND RESULTING MECHANICAL PROPERTIES OF SEAWATER MIXED CONCRETE

by

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B.S, Civil Engineering, Istanbul Technical University, 2017

Submitted to the Institute for Graduate Studies in

Science and Engineering in partial fulfillment of

the requirements for the degree of

Master of Science

Graduate Program in Civil Engineering

Boğaziçi University

2020

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere appreciation to my thesis advisor Prof. Dr. Nilüfer ÖZYURT ZİHNİOĞLU for her guidance, invaluable support, kindness and scientific advice throughout the duration of the thesis. I would also like to thank my thesis co-advisor Dr. Abdullah Huzeyfe AKCA for his support, insightful comments, suggestions, and guidance. I would like to thank Prof. Dr. Turan ÖZTURAN for his comments and suggestions.

I would like to thank my thesis committee members Assoc. Prof. Özkan ŞENGÜL and Assoc. Prof. Sezen SOYER UZUN for their interest and sparing time in examining my thesis.

I am very grateful to my friend and lecturer at İstanbul Aydın University Senem BİLİCİ and our Construction Material Laboratory fellow, Ümit MELEP for his help, technical assistance and patience during the experiments. Furthermore, I would like to thank my colleagues and friends, Elifsu BALCI, Onur ÖZTÜRK, Hasan YILDIRIM and Filiz TATLILIOĞLU, for their help during my thesis project. I am also grateful to Boğaziçi University BAP – Scientific Research Projects for their financial support. (Project Code: 14861)

Finally, I dedicate my thesis to my beloved wife Özge ÜNLÜTÜRK AYDOĞAN, my dear parents Dilek AYDOĞAN and Faruk AYDOĞAN, and my dear brother Yiğit Orkun AYDOĞAN for their love, encouragements, and supports. I would like to express how I am fortunate to have them.

To my lovely family…

ABSTRACT

MICROSTRUCTURAL DEVELOPMENT AND RESULTING MECHANICAL PROPERTIES OF SEAWATER MIXED CONCRETE

According to the “Water Report” published by United Nations in 2018 (UN World Water Report, 2018), two thirds of the world’s population live in areas that experience water shortage for some time in a year. Ongoing studies and predictions represent that water shortage problem will increase in the near future. Based on that information, many researchers worldwide focus on the subjects such as waste water management, use of seawater for several applications and etc., under the scope of sustainability. Construction industry is represented as one of the moderately water dependent sectors in the “2016 Water Report” (UN World Water Report, 2016) of United Nations. Concrete sector is also one of the big water consumer sectors, since concrete is the most used construction material worldwide. In the scope of this study, the main objective was to understand microstructural development and resulting mechanical properties of seawater concrete. Most of the studies found in literature focused on changes in mechanical behavior when seawater was used as the mix water for concrete. However, the number of studies that examine and explain the reason for changes in mechanical behavior is yet very limited. 8 different concrete mixtures were produced in the scope of this study. Type of mix water (seawater and tap water) and type of cement (PC and Sulfate resisting cement) were varied. Macro synthetic structural fibers were also used to see the effectiveness of these fibers when combined with seawater mixed concrete. Detailed microstructural analyses were carried out as well as mechanical strength tests to understand and evaluate the reasons for changes in the material behavior when seawater was used as the mix water for concrete.

ÖZET

DENİZ SUYU İLE ÜRETİLMİŞ BETONUN MEKANİK SONUÇLARI VE MİKRO YAPISAL GELİŞİMİ

Birleşmiş Milletler tarafından 2018 yılında yayınlanan “Su Raporu” na (BM Dünya Su Raporu, 2018) göre, dünya nüfusunun üçte ikisi yılın bazı zamanlarında su sıkıntısı çeken alanlarda yaşıyor. Devam eden çalışmalar ve tahminler, su kıtlığı sorununun yakın gelecekte artacağını göstermektedir. Bu bilgilere dayanarak, dünya çapında birçok araştırmacı, sürdürülebilirlik kapsamında atık su yönetimi, çeşitli uygulamalar için deniz suyunun kullanımı vb. gibi konulara odaklanmaktadır. İnşaat sektörü, Birleşmiş Milletler'in “2016 Su Raporu” nda (BM Dünya Su Raporu, 2016) orta derecede suya bağımlı sektörlerden biri olarak temsil edilmektedir. Bu sektör, beton dünya çapında en çok kullanılan inşaat malzemesi olduğu için, aynı zamanda büyük su tüketici sektörlerinden biridir. Bu çalışma kapsamında temel amaç, deniz suyu betonunun mikroyapısal gelişimini ve bunun sonucunda ortaya çıkan mekanik özelliklerini anlamaktı. Literatürde bulunan çalışmaların çoğu, deniz suyu beton için karışım suyu olarak kullanıldığında mekanik davranıştaki değişikliklere odaklanmıştır. Bununla birlikte, mekanik davranıştaki değişikliklerin nedenini inceleyen ve açıklayan çalışma sayısı henüz çok sınırlıdır. Bu çalışma kapsamında 8 farklı beton karışımı üretilmiştir. Karışım suyu olarak deniz suyu ve musluk suyu, çimento tipi olarak Portland çimentosu ve Sülfata dayanıklı çimento kullanılmıştır. Makro sentetik yapısal lifler, deniz suyu ile üretilmiş betonlardaki etkinliğini görmek için kullanılmıştır. Beton için karışım suyu olarak deniz suyu kullanıldığında malzeme davranışındaki değişikliklerin nedenlerini anlamak ve değerlendirmek için detaylı mikroyapı analizleri ve mekanik testleri yapılmıştır.

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1. INTRODUCTION

According to the United Nations World Water Report 2018, two-thirds of the world population are suffering from water shortages. In terms of the studies and estimates, the problem will be increasing year by year. Construction industry is a sector that huge amount of fresh water is used for production concrete, cleaning, curing etc. Therefore, this sector contributes to the water shortages.

To use freshwater sustainably, seawater can be used as mixing water in concrete. Since seawater contains high amount of chloride ions and these ion leads to corrosion of steel reinforcements, it is prohibited to use in concrete by standards. Nonetheless, seawater concrete may be used for the non-reinforced concrete applications. In addition, the usage of polymer based reinforcements is spreading. It is believed that the use of fresh water will decrease significantly in concrete industry by using seawater as mix water in concrete for some applications. Moreover, many regions, such as islands, cannot reach the fresh water in their own territories and they must transport it. This process creates high cost and CO_2 emissions. The use of seawater as mix water in concrete in these areas reduces cost of constructions and CO_2 emission.

Huge amount of freshwater is used annually for mixing, curing, and cleaning. Possibility of the use of seawater as the mixing water in concrete should be seriously investigated to save freshwater. Using seawater as mixing water in concrete has been investigated since 1970s; however, most of them focused on only mechanical properties at early ages. There was not enough extensive researches on the effect of seawater as mix water on the concrete properties. The number of published articles on the use of seawater as the mixing water in concrete from 1974 to 2019 was given in Figure 1.1. In recent years, interest in the subject has increased with the effect of decreasing water resources and climate change. Most of the research studies focused on the effect of the seawater on the mechanical properties. The studies that focused on long term durability and microstructure were limited.

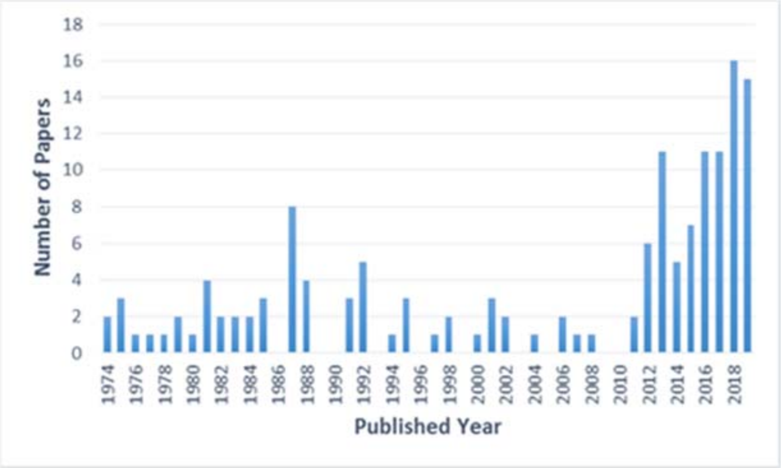


Figure 1.1. Number of articles published from 1974 to 2019 on the use of seawater as the mixing water in concrete (*The data from 1974-2013 was taken from the study of Nishida et al. [1])

1.1. The Effects of the Using Seawater as the Mix Water in Concrete

Mohammed et al. [2] investigated concrete specimens for 20 years under the tidal environment. They reported that the early strength of the seawater concrete was higher than the strength of tap water concrete. They stated that use of seawater as mix water in concrete provided early strength development due to the acceleration of chloride ions in seawater. Nevertheless, the compressive strength results were found to be similar for seawater and freshwater concrete at later ages.

Wegian [3] used seawater as mixing and curing water. He studied the effects of seawater on the mechanical properties of concrete. Curing was applied until the test ages. As a result of this study, he found that the strength was higher in the samples cast using seawater as the mixing water and cured in the seawater at early ages (7th day and 14th day); on the other hand, the reduced strength was observed at later ages (28th day and 90th day). They stated that reduction increased in strength with increasing exposure time and attributed this to the salt crystallization formation. Besides, they reported improved resistance of concrete against seawater and saline solutions when they used Sulfate Resisting Cement in concrete.

Younis et. al. [4] studied the effect of seawater on the fresh and hardened state properties of concrete produced with OPC up to 56 days. In that study, seawater and tap water were used for mixing and curing. Tap water curing and seawater curing last up to 28 and 56 days, respectively. They found slightly higher compressive and tensile strength at early ages for the specimens produced with seawater than those of the specimens produced by tap water. However, they stated that strength of the tap water concrete was higher than the strength of seawater concrete at later ages (28th and 56th days), even though permeability results were similar. Moreover, curing water type did not affect the mechanical properties of seawater concrete; nonetheless, seawater curing slightly decreased the mechanical strength of concrete specimens made by tap water when compared to the concrete specimens cured in tap water.

1.2. The Effects of Using Supplementary Construction Materials (SCMs) in Seawater Concrete

Some researchers studied the effect of use of seawater with the addition of supplementary cementitious materials (SCMs). SCMs were generally used for two main purposes in seawater concrete; to improve final strength due to pozzolanic reactions and bind chloride ions owing to formation of Friedel’s salt (FS). Thomas and his co-workers [5] investigated the effect of SCMs on chloride binding. They stated that SCMs improved the chloride binding of the paste as a result of Friedel’s salt formation and higher alumina content of SCMs increased the chloride binding capacity. Cheng et. al. [6] investigated addition of metakaolin(MK) and ground granulated blast furnace slag(GGBFS) in lightweight aggregate concrete mixed with seawater.

They stated that the compressive strength increased with MK and GGBFS addition and seawater mixing due to the pozzolanic reaction and the acceleration effect of seawater. They mentioned that chloride binding capacity increased by increasing Friedel's salt formation. Even though Friedel's salt was detected in all concrete specimens mixed with seawater, they showed that Friedel's salt formation increased due to the addition of MK and GGBFS. Shi et al. [7] reached to the similar results in their study. They mentioned that Friedel's salt formation increased by increasing MK. The chloride binding improvement depended on the alumina content of SCMs.

Nonetheless, Talero et. al. [8] stated that total aluminum content in SCMs was not important to form Friedel's salt. They emphasized that reactive alumina content, which was shown as $Al_2O_3^{r-}$ in that study, was the main parameter. Two different types of Portland cement (Ordinary Portland cement and Portland cement with low C_3A) and six different SCMs were used. Fresh water was used as the mix water. 14 different types of blends were produced. They were stored in NaCl solution and Friedel's salt formations were observed via XRD analyses up to 720th day. According to results, they concluded that in the blends, which were produced by using OPC and pozzolans, the origin of the formation of FS was mainly C_3A in OPC and $Al_2O_3^{r-}$ in pozzolans. However, in the blends, which were produced by using PC with low C_3A and pozzolans, the origin of the formation of FS was mainly $Al_2O_3^{r-}$ in pozzolans due to lack of C_3A content in PC. In addition, they deduced that higher reactive alumina content in SCMs improved chloride binding capacity due to the formation of FS.

Several research projects were performed about that topic. Seacon project, which was supported by European Union Horizon Program, could be good example. In this project, the researchers investigated the effects of seawater (as the mixing water), salt-contaminated aggregate and cement on the non-corrosive reinforced concrete. It was reported that two real size structures will be built and these structures will be monitored continuously in different climatic conditions for this project. Many studies have been done within the scope of this project. Federica and his co-workers contributed to this project. Federica et. al. [9] used 4 different mixes, which were Portland cement + limestone (as named reference cement) + fly ash and tap water concrete (Mix 1), Portland cement + chloride contaminated limestone (as named Seacon cement) + fly ash and tap water concrete (Mix 2), Portland cement + limestone + fly ash and seawater concrete (Mix 3) and Mix 1 + recycled concrete aggregates (Mix 4). It was seen that seacon cement showed shorter setting time than reference cement due to the abundance of chloride content. Moreover, the compressive strength was measured until 90th day. They stated that even tough compressive strength of all concrete samples were similar at 28th day, the compressive strength of Mix 2 and Mix 3 was lower than Mix 1 and Mix 4 at 90th day. In addition, they carried out XRD-Rietveld analysis on their pastes. Friedel's salt formation was observed in only Mix 3. The amount of ettringite formation was similar for Mix 1 and Mix 3. This result was attributed the lack of sulfate ions in Mix 3 to produce more ettringite crystals. Besides, the amorphous phase (mainly C-S-H) was similar for all pastes.

Li et. al. [10] tried to understand the effect of seawater in low water to binder ratio pastes made by silica fume and/or slag at early age. Their research involved the first 72 hours. Friedel's salt was detected in their samples made by seawater. They reported the possible chemical reactions to form Friedel's salt. They also reported that addition of slag increased the formation of Friedel's salt due to the high alumina content. The possible reaction mechanisms of FS formation as follows;

$$Ca(OH)_2+C_3A.CaSO_4.14H_2O + Cl^- \rightarrow C_3A.CaCl_2.10H_2O \text{ (Friedel's salt)} \qquad (1.1)$$

$$C_3A.Ca(OH)_2.12H_2O + Cl^- \rightarrow C_3A.CaCl_2.10H_2O \qquad (1.2)$$

$$C_3A.CaCO_3.10H_2O + Cl^- \rightarrow C_3A.CaCl_2.10H_2O \qquad (1.3)$$

$$C_3A + CaCl_2 + 10H_2O \rightarrow C_3A.CaCl_2.10H_2O \qquad (1.4)$$

$$C_3A + C_3S + 2NaCl + 15H_2O \rightarrow C_3A.CaCl_2.10H_2O + C_2S.4H_2O + 2NaOH \qquad (1.5)$$

$$3Ca(OH)_2 + CaCl_2 + Al_2O_3 + 7H_2O \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O \qquad (1.6)$$

According to these equations, it could be seen that C_3A and/or its products, $Ca(OH)_2$ and $CaCl_2$ could be consumed to form Friedel’s salt. Moreover, more aluminum content could improve the formation of FS according to Equation 1.4. The contribution of pozzolans on the formation of FS could be controversial because they decreases C_3A content; however, they increases the aluminum content in the concrete. The balance between C_3A and aluminum content of blended cements is the key factor to formation of FS.

Katano et al. [11] investigated the effects of seawater as mix water and unwashed sea sand as aggregate in the concrete. They used some supplementary cementitious materials (fly ash, slag, silica fume) with different ratios and Portland cement as a binder. They reported higher compressive strength for the specimens produced by using seawater, especially at early ages. They attributed this result to the accelerating effect of chlorides. However, the difference was found to be insignificant at later ages.

Portland cement, and its combinations with fly ash and blast furnace slag were used as binder material and seawater was used as mix water by Otsuki et al. [12]. The produced samples were exposed to tidal environment from 1 week to 20 years. Compressive strength tests were performed periodically during this time. They observed that the strength difference between seawater concrete and fresh water concrete was less than ±10%. They concluded that seawater did not affect compressive strength significantly.

Bhaskar et al. [13] used different ratios of fly ash and GGBS with Portland cement. They reported that the strength of seawater specimens was higher than the strength of tap water specimens especially at early ages for all binders (OPC, OPC+FA, OPC+GGBS). They also reported decrease in strength for FA and GGBS added concretes when compared to OPC concretes for the 1st 28 days.

Li et al. [14] produced seawater and fresh water concrete samples. Portland cement and metakaolin were utilized. The compressive strength were measured until 56th day. They concluded that strength of seawater concrete at early ages (3rd and 7th day) was higher than strength of fresh water concrete due to the presence of chloride. In the following days, it was observed that the rate of increase was decreased due to the binding of chloride ions by metakaolin and cement.

Erniati and his coworkers [15] studied Self Compacting Concrete (SCC) made by using seawater and freshwater. The binder was Portland Composite Cement. They reported that even the seawater specimens showed good workability and met standards, the fresh state properties of tap water concrete (slump flow and T50 time) were better. The strength was measured until 90th day. Early strength of concrete made by using seawater was higher; however, strength of later ages were similar.

Many researchers stated that seawater increased the early age strength due to the acceleration effect of Cl^- ions; however, the later age strength was similar to that of tap water concrete. If the studies given above was considered, it was seen that the above statement was also generally valid for the concretes made by using supplementary cementitious materials.

1.3. The Possible Effects of the Using Seawater as the Mix Water on the Microstructure of Concrete

From the given literature above, most of the studies resulted that seawater improved the early age strength. Seawater can accelerate the reactions depending on the NaCl content in the water. According to Younis et. al.[4], seawater accelerated the hydration reactions due to the formation of $CaCl_2$. They stated that NaCl in seawater reacted with Portlandite and then $CaCl_2$ was formed. $CaCl_2$ is known as an accelerator.

$$Ca(OH)_2+2NaCl \rightarrow CaCl_2+2Na^++2OH^- \tag{1.7}$$

In most of the studies related to the seawater as the mixing water, early strength and 28-day strength were only examined. It is obvious that the durability of the concrete produced by using seawater is also very important. Seawater contains not only high amounts of Cl^- ions but also high amounts of SO_4^- ions. Therefore, the effect of these ions should be investigated to explain strength development.

Sulfate attack can be categorized as internal sulfate attack and external sulfate attack. External sulfate attack is well-known. In that condition, concrete interacts with soil and ground water which contains sodium, magnesium, calcium and potassium sulfates. These ions can attack to concrete and react with remaining C_3A and/or its products. The products (ettringite, gypsum, anhydrate etc.) of these reactions can damage the concrete. However, internal sulfate attack is a relatively new topic. In that condition, ettringite crystals are formed at hardened stage without any sulfate attack externally. For this study understanding the effects of internal sulfate attack was important since sulfate ions were introduced into concrete by using seawater as the mixing water. According to Ali's study [16], there are two internal sulfate attack mechanisms, which lead to the Delayed Ettringite Formation;

- Decomposition of ettringite crystals at high temperature and reformation of ettringite at room temperature
- Late sulfate release and formation of new ettringite crystals at hardened stage

For seawater concrete, second mechanism can occur. As it is known that seawater contains much more sulfate ions than tap water. Some of these ions can be released at later ages, and damage concrete microstructure.

Ramezanianpour et. al. [17] published a review article about the combined effects of Sulfate-Chloride attack on concrete. They stated that the effect of separate attacks of these ions was different than the combined attacks. The effect of chloride ions on sulfate attack and the effect of sulfate ions on chloride attack were discussed. Many researches in that study stated that Cl^- ions decreased the negative effect of sulfate ions. This mitigating effect was attributed to depletion of C_3A and/or its products to form Friedel's salt by excessive chloride ions, and higher penetration and reaction rate of chloride ions.

Lee et. al. [18] produced OPC and OPC+SF concrete and immersed them into sulfate solution and sulfate + chloride solution. They observed the specimens for 510 days. The strength of concrete in combined solution was better than concrete in a sulfate solution. Friedel's salt was detected on XRD graphs of the specimens, which were immersed in sulfate + chloride solution. They resulted that Cl^- ions mitigated the negative effect of sulfate ions, especially for OPC concrete. They attributed this effect to;

i. The ettringite formed in the combined solution might be less expansive.
ii. Friedel's salt formation as a result of the reaction of chloride ions and C_3A.

They stated that the rates of diffusion of chloride and sulfate ions were different. Chloride ions can penetrate and react with C_3A and its products form quicker than sulfate ions. Hence, presence of chloride ions mitigated the negative effect of sulfate damaging.

According to Stroh et. al. [19], the mechanism of the combined sulfate-chloride attack was as follows;

1. Alumina products bind Cl^- ions and the resulting product is Friedel's salt
2. SO_4^- ions react with portlandite and form gypsum, anhydrate, and decrease pH of concrete
3. Low pH causes to depletion of Friedel's salt
   The stability of Friedel's salt is sensitive to pH alteration. If pH value decreases, Friedel's salt can transform to its constituents (alumina products).
4. Excessive sulfate ions create ettringite.
   After decomposition of Friedel's salt, excessive sulfate ions in the matrix can react with alumina products and form ettringite crystals. These crystals at the hardened stage can damage the concrete.

Although the effect of ettringite formation at hardened stage is well known, the effect of gypsum formation on concrete is still controversial. As it is know that portlandite content is the key factor for formation of gypsum. The reaction mechanism is:

$$Ca(OH)_2+XSO_4 \rightarrow CaSO_4.2H_2O+X(OH)_2 \tag{1.8}$$

Tian et. al. [20] published an article to demonstrate the effect of gypsum formation on concrete. They presented the literature review and their own study. According to their literature review, most of the studies resulted that the formation of gypsum could cause expansion due to internal tensile stresses, like ettringite formation. A few literatures in that study resulted that gypsum formation could not cause any expansion and any damage except softening effect. In their own study, they used two different kinds of C_3S with or without silica fume to minimize the formation of the ettringite. They created two different sulfate solutions: Na_2SO_4 and $(NH_4)_2SO_4$ and measured the expansion of paste and mortar specimens periodically. They observed expansion for pastes and mortars without silica fume. It was resulted that the presence of silica fume minimized the expansion due to the consumption of portlandite crystals in pozzolonic reactions. These expansions were attributed to the formation of gypsum. XRD analyses were also performed in that study. The main product was found to be gypsum for all pastes. The amount of gypsum was decreased due to the addition of silica fume according to XRD results.

Gonzalez et. al. [21] used low-C_3A Portland cement with for different C_3S content (from 40% to 74%). Four different pastes were exposed to $NaSO_4$ solution and observed for two years. The expansions were measured and XRD analyses were conducted periodically. It was observed that the expansion increased by increasing C_3S content. This expansion was attributed to the gypsum formation. The XRD results of this study was given in Figure 1.2. The most gypsum formation was observed in the paste with 74% C_3S. In addition, ettringite crystals were observed for all pastes, even the cement had low C_3A content. The ettringite formation in low C_3A Portland cement pastes was attributed to the presence of ferroaluminate phases.

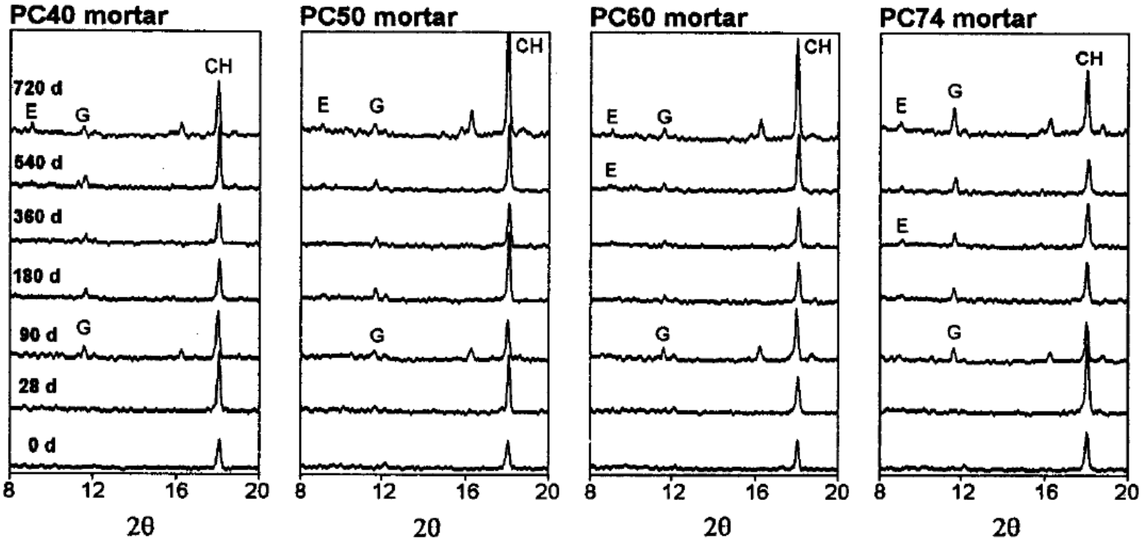


Figure 1.2. XRD results of Gonzalez et. al. [21]

1.4. The Mechanical Effect of Macro-synthetic Fibers in Concrete

The conventional reinforcement should not be used in concrete made with seawater due to the chloride abundance. However, fiber reinforced polymer bars and synthetic fibers are durable against chloride ions. For some applications such as pavements, industrial floors non-structural elements, synthetic fibers are a good option to provide ductility and some mechanical improvements. Fallah and Nematzadeh [22] used macro - polymeric fibers (MP) in different amounts (0.25% - 0.50% - 0.75% - 1.0% - 1.25%) and micro-sized polypropylene fibers (PP) in different amounts (0.1% - 0.2% - 0.3% - 0.4%- 0.5%) in their study. It was concluded that elastic modulus and splitting tensile strength were increased by increasing amount of macro fibers.

Kazmi et. al. [23] investigated mechanical performance of macro-synthetic virgin polypropylene based fiber reinforced recycled aggregate concrete (RAC). They produced concrete beams with three different replacement ratios of recycled aggregate and three different dosages of macro fibers by volume (0, 0.5%, 1%). Post-peak mechanical improvement was detected due to the fibers. They stated that normal concrete and RAC without fibers showed brittle fracture, however adding fibers provided ductile behavior. According to their SEM images, good adhesion bond between fibers and matrix was reported. They concluded that residual flexural tensile strength and toughness developed with the increase in dosage of macro-synthetic fibers for both normal and recycled aggregate concrete due to the good bond between fibers and matrix.

In that study, the effect of seawater on the mechanical and microstructural properties of concrete presented. To understand the mechanical properties, compressive strength, flexural strength, and elastic modulus test were done. Comprehensive XRD and SEM analyses were conducted to explain the mechanical behavior of this concrete.

2. EXPERIMENTAL STUDY

2.1. Materials

2.1.1. Cement and Admixture

Portland Cement (CEM I 42.5R) and Sulfate Resistant Cement (CEM IV/B) were utilized as binder materials in that study. Cement compositions were shown in Table 2.1.

Table 2.1. Cement compositions

Chemical Test Results		
Compounds	**PC**	**SRC**
Al_2O_3 (%)	5.58	6.70
Fe_2O_3 (%)	3.32	4.45
CaO (%)	63.67	53.97
MgO (%)	1.25	1.61
Na_2O (%)	0.21	0.57
K_2O (%)	0.68	0.85
SiO_2 (%)	19.63	26.15
SO_3 (%)	3.23	2.56
Cl^- (%)	0.04	0.03

A polycarboxylic ether based admixture, the density of which was 1.08 g/cm^3, was used as the superplasticizer (SP). It was utilized in the mixes in order to achieve S4 slump class, according to EN 206.

2.1.2. Aggregates

Crushed sand, natural sand and two coarse aggregates were utilized in this study. The sieve analysis was performed according to TS 802. The sieve analysis of the mix of aggregates was shown in Figure 2.1.

The mineralogical properties of No.2, No.1 and crushed sand were the same. The difference was only size. The mineralogical properties of aggregates were shown in Table 2.2. Moreover, the XRD result of crushed stone (No.2, No.1 and crushed sand) was given in Figure 2.2.

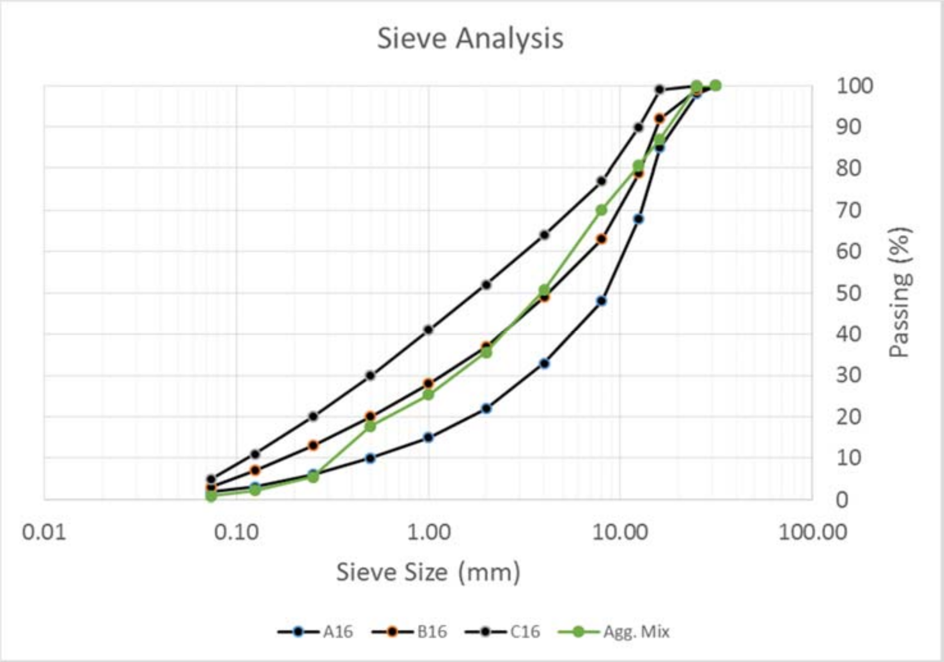


Figure 2.1. Gradation curve of the mix of the aggregates

Table 2.2. Mineralogical properties of aggregates

Minerals	No.2 Crushed Stone	No.1 Crushed Stone	Crushed Sand	Natural Sand
Quartz	85-90%	85-90%	85-90%	88-92%
Feldspar	4-5%	4-5%	4-5%	2-3%
Calcite	4-8%	4-8%	4-8%	2-3%

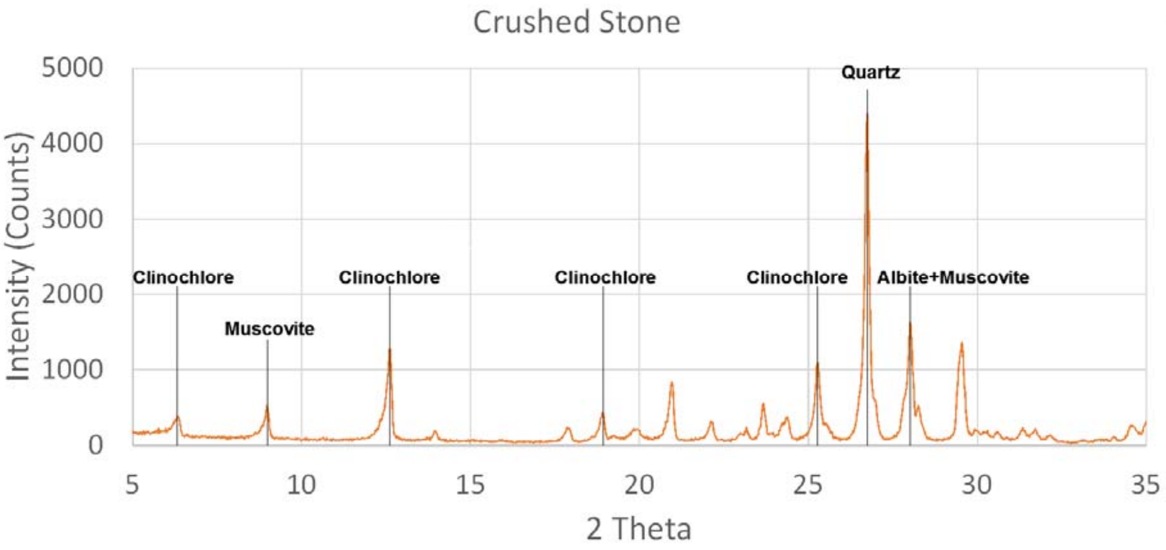


Figure 2.2. XRD result of crushed stone

2.1.3. Water

Seawater and tap water were used as the mix water. The seawater was brought from the Black Sea in Sarıyer, Istanbul. Chemical characterizations of mix waters and corresponding standards were given in Table 2.3.

Table 2.3. Chemical characterization of the two types of mixing water

Compounds	Results (mg/L)		Method/Standard	
	Tap Water	Seawater	Tap Water	Seawater
Sodium (Na)	24	4420	SM 3111 B	SM 3111 B
Potassium (K)	4	193	SM 3111 B	SM 3111 B
Calcium (Ca)	52	234	TS 6228, EN ISO 7980	TS 6228, EN ISO 7980
Magnesium (Mg)	8	638	TS 6228, EN ISO 7980	TS 6228, EN ISO 7980
Chloride (Cl)	40	10068	SM 4110	TS 4164, ISO 9297
Sulfate (SO_4)	77	1178	SM 4110	TS 5095
Organic Substance	Appropriate	Appropriate	TS EN 1008	TS EN 1008
pH	7.06	8.61	TS EN ISO 10523	TS EN ISO 10523

2.1.4. Fiber

For this study, structural macro polypropylene-based fibers were used in the mixes. The length and diameter of the fibers were 40 mm and 0.72 mm respectively (l/d=55.6). Tensile strength of the fiber was 550 MPa.

Figure 2.3. Fibers used in that study

2.2. Mix Design

In this study, concrete mixes were prepared by using two different cement types, Ordinary Portland Cement, and Sulfate Resistant Cement (SRC), and both fibrous (0.5 % vol.) and non-fibrous samples were produced. Seawater and tap water were used as the mix water for concrete. Water-to-cement ratio was taken to be 0.45. A polycarboxylic ether based admixture was used in all mix types in order to achieve S4 slump class. All the mix proportions were shown in Table 2.4.

Table 2.4. Mix proportions

Codes	**Ingredients (kg/m^3)**							
	Cement	**Water**	**Natural Sand**	**Crushed Sand**	**No.1**	**No.2**	**SP**	**Fiber**
PC TW NF	410	184	280	661	563	378	2.91	-
PC TW F	410	184	280	661	563	378	3.88	4.5
PC SW NF	410	184	280	661	563	378	2.91	-
PC SW F	410	184	280	661	563	378	3.47	4.5
SRC TW NF	410	184	280	661	563	378	5.37	-
SRC TW F	410	184	280	661	563	378	5.41	4.5
SRC SW NF	410	184	280	661	563	378	4.92	-
SRC SW F	410	184	280	661	563	378	5.41	4.5

All specimens were cured in a curing tank as suggested by EN 12390-2 standard. Specimens were removed from their molds after 1 day and kept in the curing tank until the test day and/or 28th day. The temperature of curing water was set at around 20 ± 2 ^{o}C as suggested in EN 12390-2 standard.

The codes of the mixtures were also given in Table 2.5. PC and SRC referred to Portland cement and sulfate resistant cement, respectively. TW and SW represented tap water and seawater, while F and NF showed fibrous and non-fibrous specimens, respectively.

Table 2.5. The codes of the mixtures

Codes	Description
PC TW NF	Portland Cement and Non-Fibrous Concrete with Tap Water
PC TW F	Portland Cement and Fibrous Concrete with Tap Water
PC SW NF	Portland Cement and Non-Fibrous Concrete with Seawater
PC SW F	Portland Cement and Fibrous Concrete with Seawater
SRC TW NF	Sulfate Resistant Cement and Non-Fibrous Concrete with Tap Water
SRC TW F	Sulfate Resistant Cement and Fibrous Concrete with Tap Water
SRC SW NF	Sulfate Resistant Cement and Non-Fibrous Concrete with Seawater
SRC SW F	Sulfate Resistant Cement and Fibrous Concrete with Seawater

2.3. Experimental Methods

2.3.1. Fresh State Tests

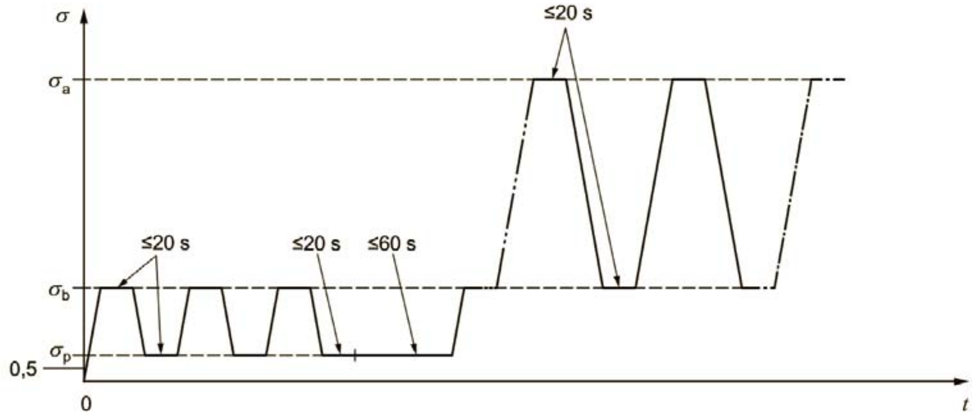
2.3.1.4. Slump and Density. After mixing of materials, slump tests and density measurements were conducted on fresh concrete. Slump and density of concrete were performed according to EN 12350-2 and EN 12350-6, respectively.

2.3.1.5. Setting Time. To understand the acceleration effect of seawater on the hydration reactions, setting time tests were performed according to EN 196-3. Four different type of pastes were produced: Portland cement+tap water, Portland cement+seawater, SRC+tap water and SRC+seawater pastes. For each batch, 3 specimens were used to test.

2.3.2. Hardened State Tests

2.3.2.6. Mechanical Properties. Load controlled compressive strength tests were carried out on 15 cm x 15 cm x 15 cm cube specimens according to EN 12390-3 standard at the ages of 7th, 28th, 180th and 360th days to observe strength development of the specimens. For each batch, 3 cube specimens were used to test.

Modulus of elasticity tests were performed on 10 cm x 20 cm cylindrical specimens according to EN 12390-13 / Method A (Determination of Initial and Stabilized Secant Modulus of Elasticity) at the ages of 7th, 28th, 180th and 360th days. The followed loading cycle was shown in Figure 2.4. This test was performed by using a MTS servo-hydraulic test machine with a maximum loading capacity of 500 kN. For each batch, at least 3 cylinder specimens were used for the tests. The test setup was shown in Figure 2.5.



Key

σ	applied stress in MPa
σ_a	upper stress → $f_c/3$
σ_b	lower stress → $0.10 \times f_c \leq \sigma_b \leq 0.15 \times f_c$
σ_p	preload stress → $0.5 \text{ MPa} \leq \sigma_p \leq \sigma_b$
t	time in s

Figure 2.4. Loading cycle of the elastic modulus test

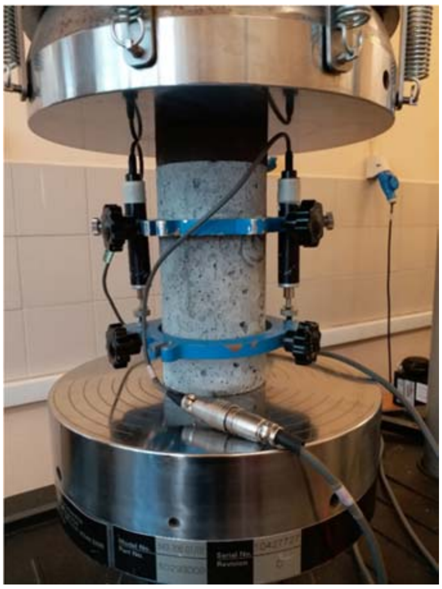


Figure 2.5. Elastic modulus test setup

CMOD controlled three – point bending tests according to JCI-S-001 and JCI-S-002 were carried out on 10 cm x 10 cm x 50 cm beam specimens at the ages of 28th, 180th and 360th days. The first standard was used for non-fibrous beams, the latter was used for fibrous beams. All beams were notched and the remaining section was 7x10 cm^2. For each batch, 3 beam specimens were used for the tests.

2.3.2.7. Microstructural Investigation. To explain the results of hardened state properties depending on the microstructure, XRD analyses and SEM investigations were performed at the ages of 28th, 270th and 360th days. The samples were taken from the beams, which were used for the flexural strength tests, and the hydration products were examined. Samples were taken from both the surface and the center of the beams for non-fibrous specimens (Figure 2.6).

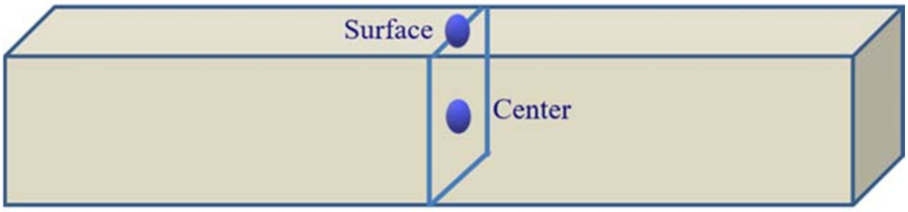


Figure 2.6. Sampling locations for SEM and XRD analysis for the non-fibrous (NF) specimens

For fibrous specimens, one sample was taken for the SEM investigation to understand the interaction between fiber and matrix.

XRD analyses were performed on the powder samples obtained from both the surface and center of the non-fibrous concrete beams. XRD analyses were conducted by A Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment located in the Bogazici University Advanced Technologies Research and Development Center.

A scanning electron microscope was used to understand the adherence between fiber and matrix. All SEM observations were conducted by FEI-Philips XL30 ESEM-FEG system located in the Bogazici University Advanced Technologies Research and Development Center electron microscopy and microanalysis unit.

3. RESULTS AND DISCUSSION

3.1. Fresh State Properties

3.1.1. Slump and Density

The slump and density values of concrete mixes were shown in Table 3.1.

Table 3.1. Fresh properties results

Codes	Slump (cm)	Density (kg/dm^3)
PC TW NF	18.5	2.44
PC TW F	20.0	2.43
PC SW NF	18.0	2.44
PC SW F	19.5	2.43
SRC TW NF	21.0	2.41
SRC TW F	21.0	2.41
SRC SW NF	19.0	2.42
SRC SW F	20.0	2.41

According to EN 206-1, all mixes were in the range of S4 slump classes. The density of all mixes were similar as expected. The type of mixing water, cement type and adding fibers did not affect the density significantly.

3.1.2. Setting Times

The average setting times of pastes were shown in Table 3.2.

Table 3.2. Setting time results

Codes	Initial Set (minutes)	Final Set (minutes)
PC TW NF	245	318
PC SW NF	225	298
SRC TW NF	415	555
SRC SW NF	353	513

According to the results, it was seen that seawater decreased the setting times. In Portland cement samples, seawater shortened the initial and final set by 8.2% and 6.3%, respectively. Moreover, in SRC samples, seawater shortened the initial and final set by 14.9% and 7.5%, respectively. This result was attributed to the formation of $CaCl_2$. $CaCl_2$ accelerated the hydration reactions and decreased the setting times [4], [10] .

3.2. Hardened State Properties

3.2.1. Mechanical Properties

3.2.1.8. Compressive Strength Test Results. For all of the 8 different mixes, three cube samples were tested for each day. Compressive strength test was performed according to EN 12390-3 standard. The values shown in Figure 3.1 were average compressive strength of the three Portland cement and sulfate resistance cement cube samples, respectively.

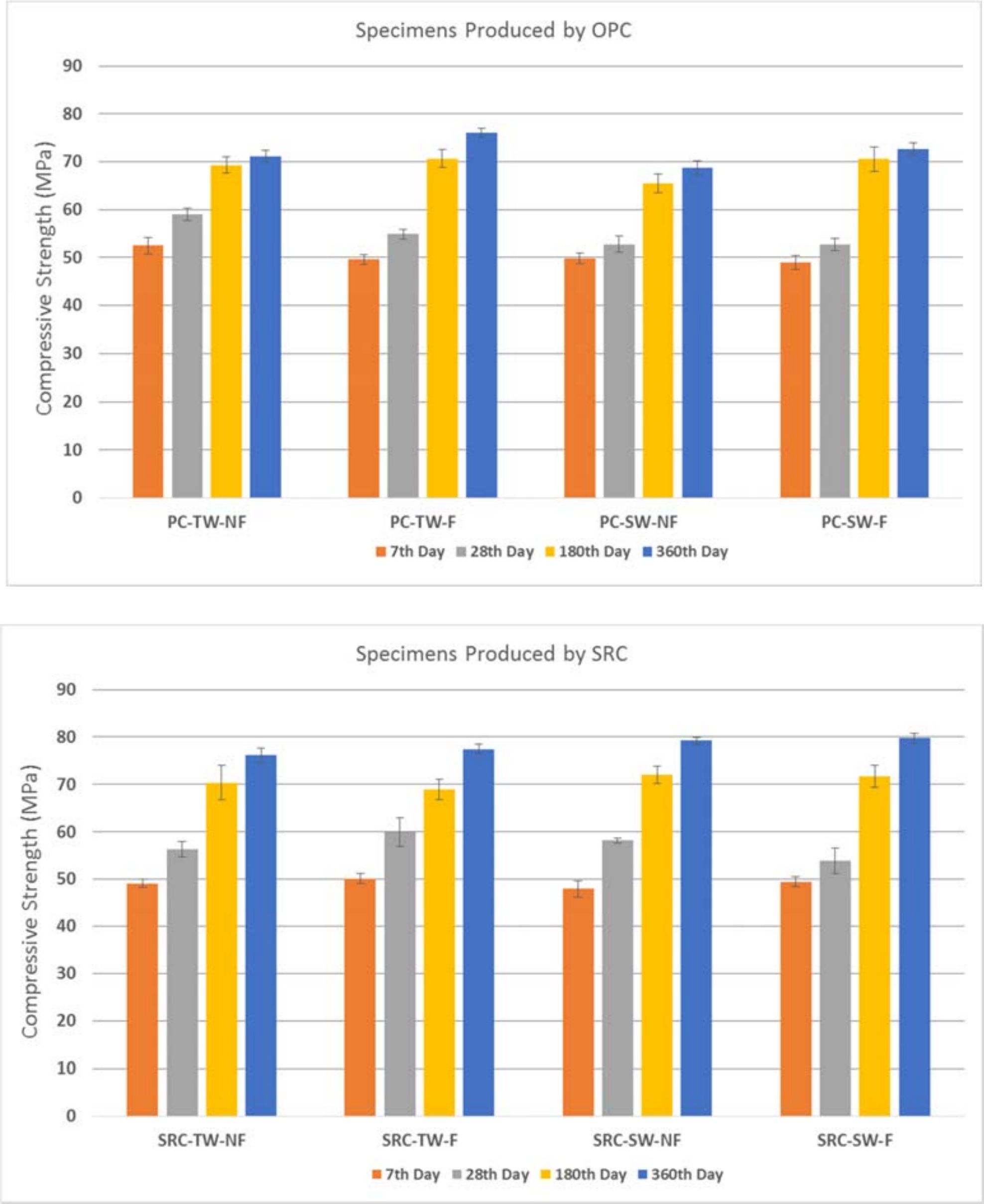


Figure 3.1. Compressive strength results of specimens

When the results were examined it could be seen that the use of seawater as the mixing water did not have a negative effect on the strength up to one year. Compressive strength results of the seawater concrete and tap water concrete samples were similar. Moreover, the 7th day strength values of the samples produced by sulfate resistant cement were relatively low compared to the samples produced by OPC most probably due to slower reactions. However, this difference was closed up to 180th day and final strength of SRC concrete was relatively higher because of the pozzolanic reactions.

In contrast to many studies, the early strength of the samples produced by seawater was not higher than tap water concrete. The accelerating effect of seawater due to formation of $CaCl_2$ depends on the Cl^- amounts in seawater as a result of Equation 1.7. Adeyemi et.al. [24] compared the concentration of ions in some of the world seas. According to their studies, Black Sea has the lowest concentration of Cl^- ions when compared to the others. Therefore; the accelerating effect of Black Sea water could differ from the others. And the ions of Black Sea in study of Adeyemi et. al. [24] were similar to Table 2.3.

Table 3.3. Concentration of ions in some seas [24]

Major Ions	Concentration (mg/L)							
	Black Sea	Marmara Sea	Mediter-ranean Sea	North Sea	Atlantic Ocean	Baltic Sea	Arab-ian Gulf	Red Sea
Sodium	4900	8100	12400	12200	11100	2190	20700	11350
Magnesium	640	1035	1500	1110	1210	260	2300	1867
Chloride	9500	14390	21270	16550	2000	3960	36900	22660
Sulfate	1362	2034	2596	2220	2180	580	5120	3050
TDS	17085	26409	38795	33060	35370	7110	66650	40960

3.2.1.9. Modulus of Elasticity Results. For all of the 8 different mixes, three cylindrical (10x20) samples were tested for each day. Elastic modulus tests were carried out in accordance with EN 12390-13 standard. The test results were shown in Figure 3.2.

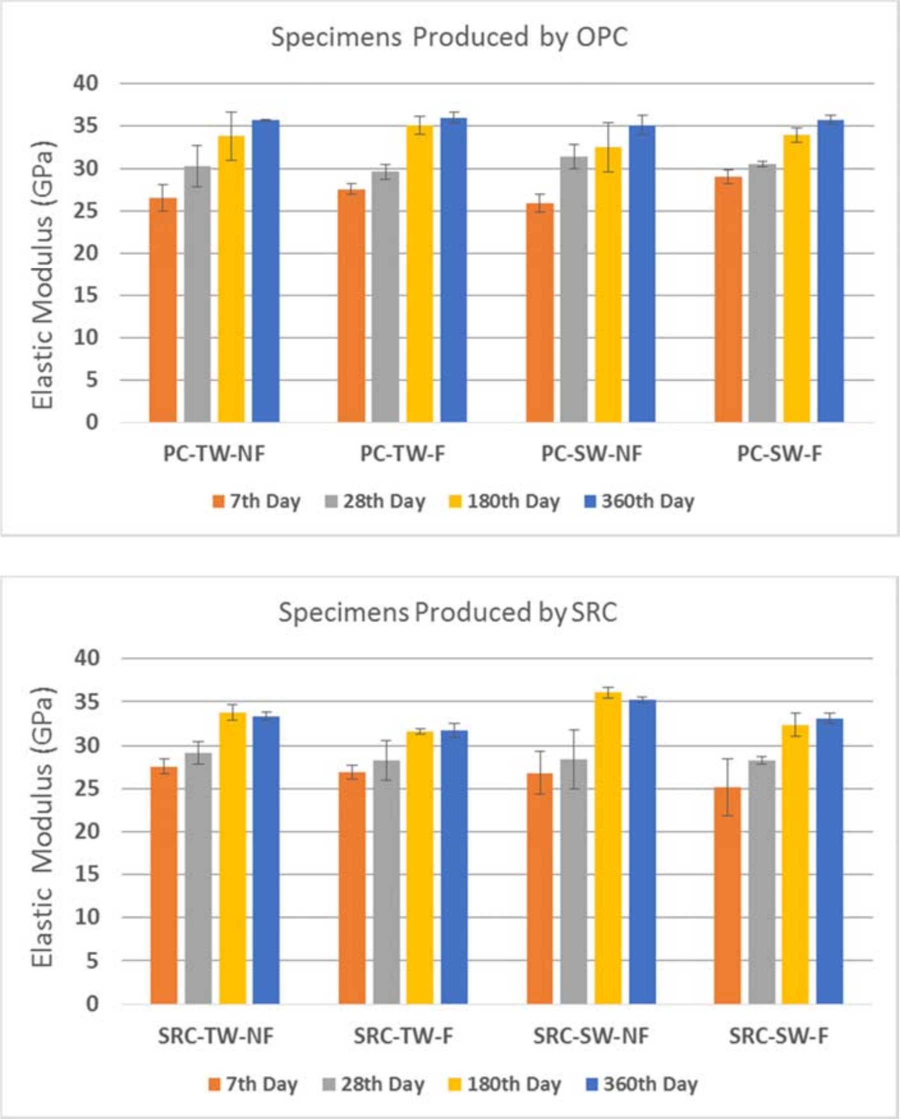


Figure 3.2**.** Elastic modulus of the samples

As shown in Figure 3.2, the type of mixing water did not affect the elastic modulus results significantly for all ages. There was no significant difference between the elastic modulus of the samples produced by seawater and the samples produced by tap water up to the first 12 months. At the same time, the fibers and cement type had no significant effect on the modulus of elasticity. The elastic modulus development of the samples was similar.

As it is known that compressive strength and elastic modulus have parallel relationship. In that study, the results of compressive strength and elastic modulus were found to be in accordance.

3.2.1.10. Flexural Test Results. For each group, crack mouth opening displacement (CMOD) controlled three – point bending tests were performed for each day. Bending tests were performed according to JCI-S-001 and JCI-S-002 standards at 28th, 180th and 360th days. The graphical results were shown Figure 3.3 for both fibrous and non-fibrous specimens. The results were summarized in Figure 3.4 and Figure 3.5.

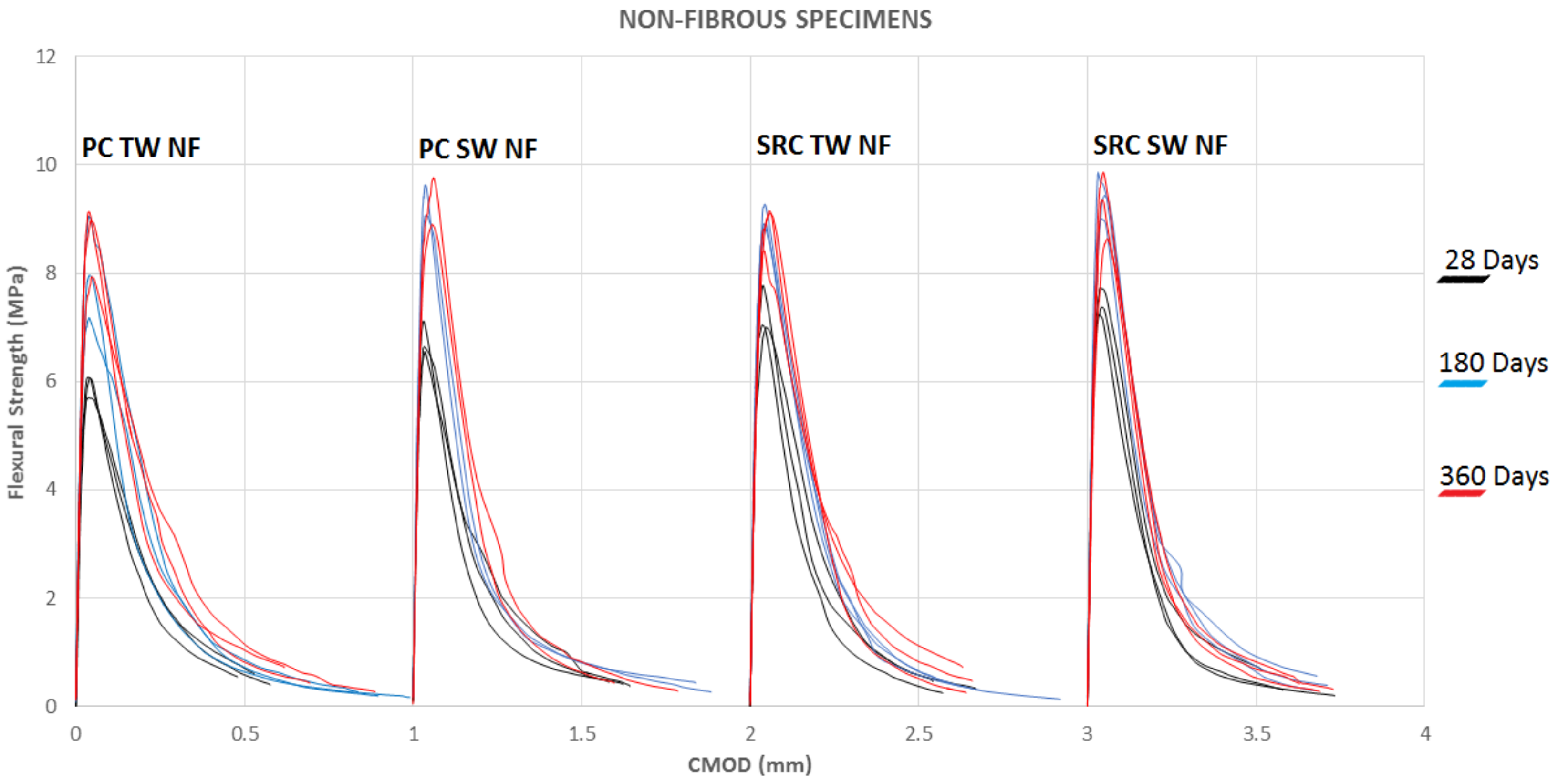


Figure 3.3. Flexural tests results

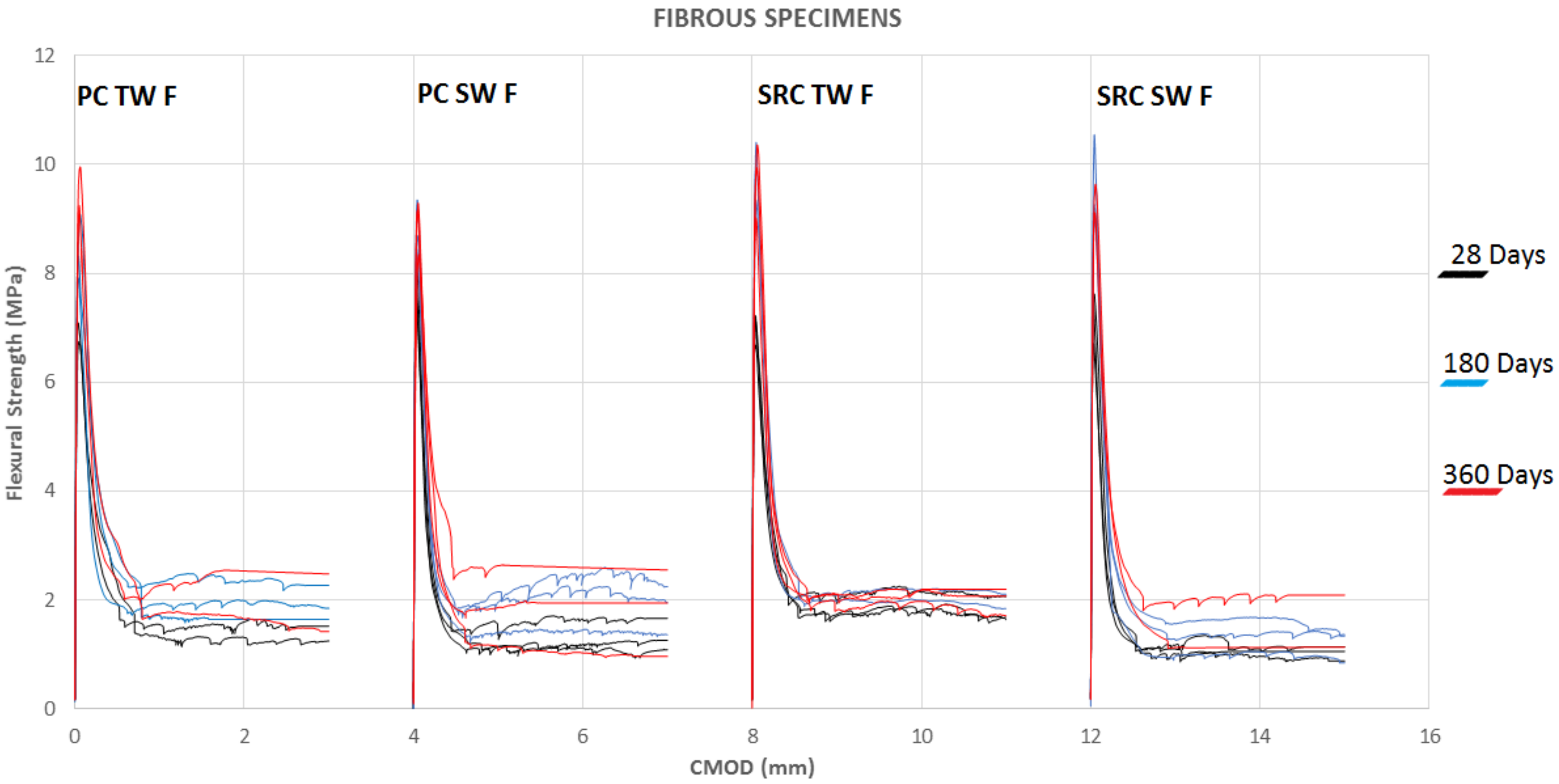
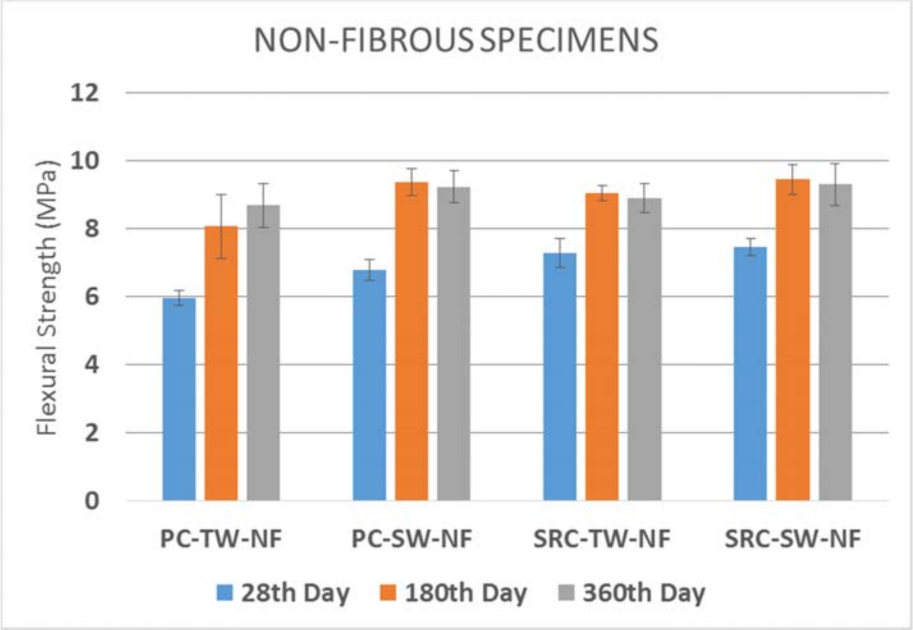


Figure 3.3. Flexural tests results (cont.)



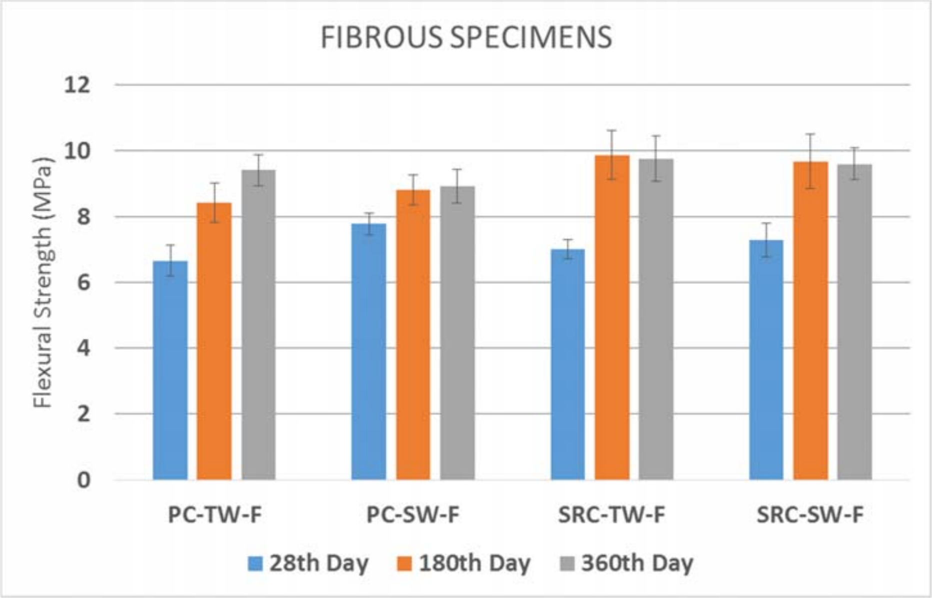
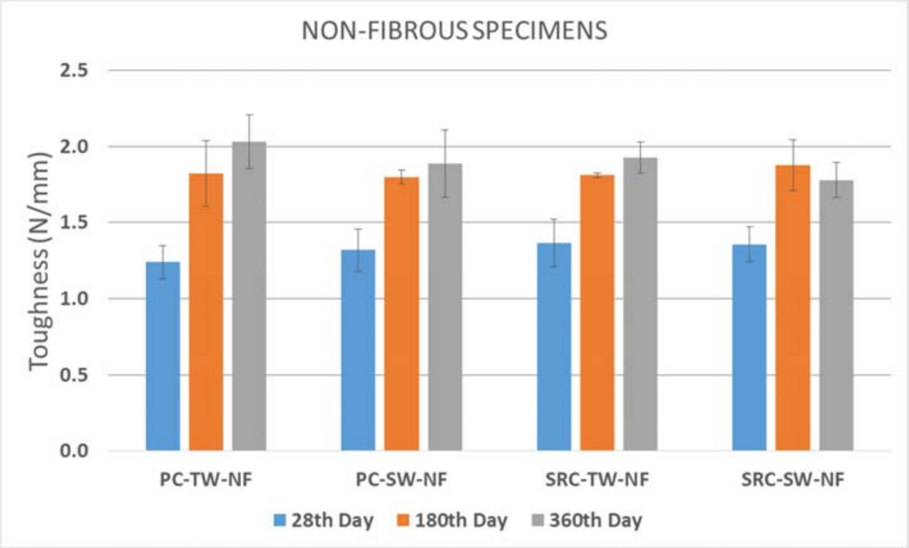


Figure 3.4. Flexural strength of the samples at 28th, 180th and 360th days



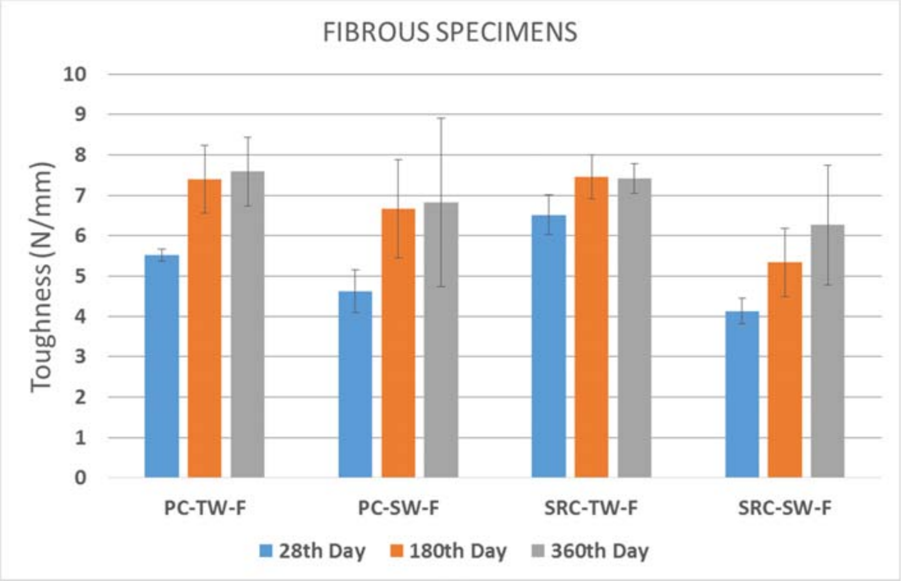


Figure 3.5. Toughness of the samples at 28th, 180th and 360th days

As can be seen from Figure 3.4, addition of fibers did not affect the flexural strength significantly for both seawater and tap water concrete. Even tough flexural strength of seawater concrete samples was relatively higher than tap water concrete samples at early ages, the ranges of strength at 360th were similar for both seawater and tap water concrete samples. At the end of the first year period, flexural strength was similar for all types of concrete samples.

On the other hand, when the toughness values were examined, it was seen that the addition of fibers increased toughness from 1.5-2.0 N/mm to 6.0-8.0 N/mm at the end of the first year period. While the toughness values of non-fibrous specimens were similar both in tap water and seawater concretes, the toughness values decreased when seawater was used in fibrous concrete. For Portland cement and fibrous concrete case, the toughness of tap water concrete was 16%, 10% and 10% higher than the toughness of seawater concrete at 28th day, 180th day and 360th day, respectively. For SRC and fibrous concrete case, the toughness of tap water concrete was 36%, 28% and 15% higher than the toughness of seawater concrete at 28th day, 180th day and 360th day, respectively. As it could be seen that the differences decreased as time passed away, especially for SRC concrete.

The mechanisms affecting the flexural strength and toughness values are different. While the flexural strength value is more dependent on the strength of the concrete matrix, the toughness value is a parameter related to the fiber-matrix adherence. Adherence between fiber and matrix was interpreted at SEM investigation section.

3.2.2. Microstructural Investigations

3.2.2.11. SEM Investigation. SEM investigations were carried out at on the samples at 28th, 270th and 360th days. Particularly in fiber samples, some indications, which could affect the post-crack behavior, was determined.

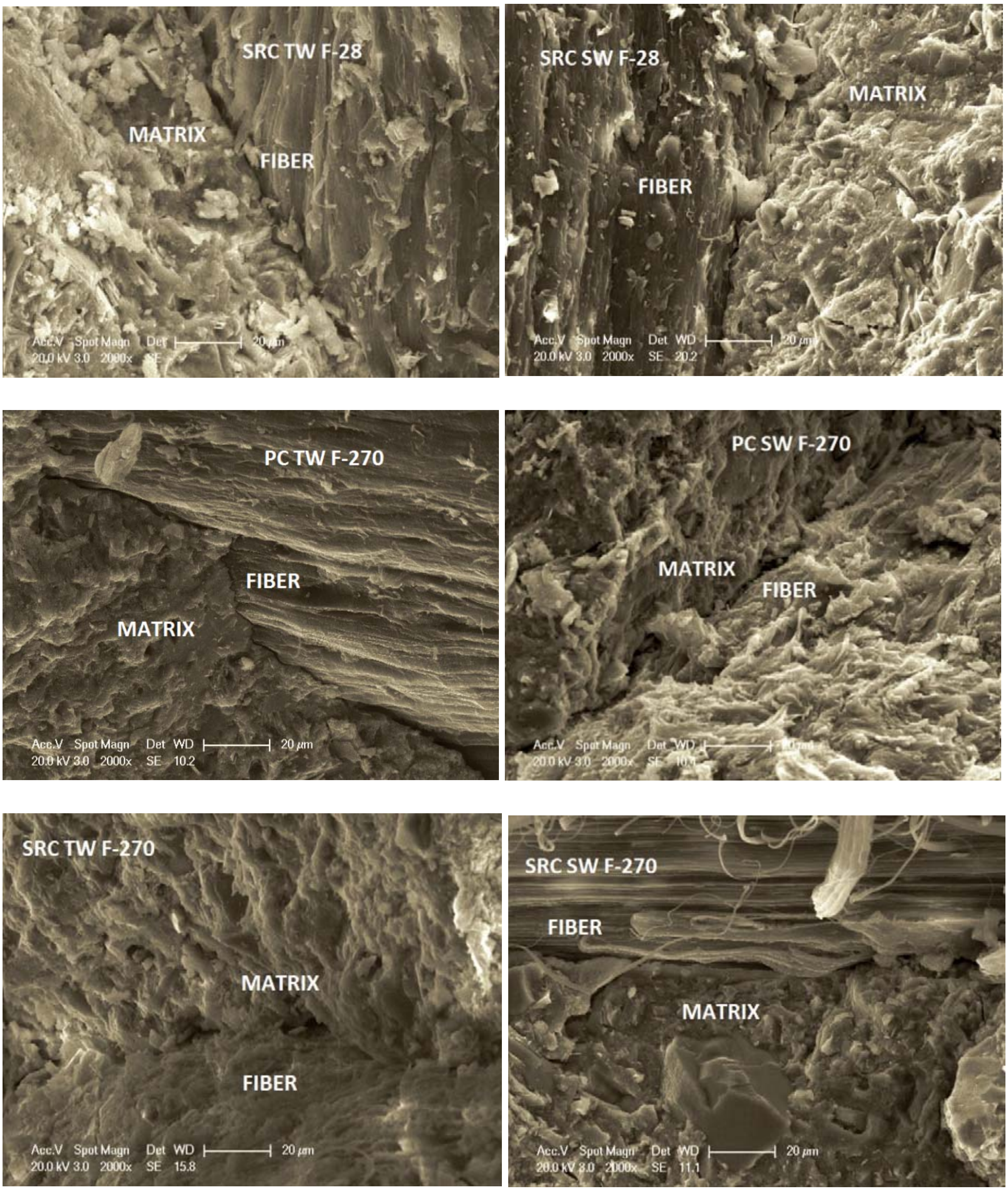


Figure 3.6. SEM pictures

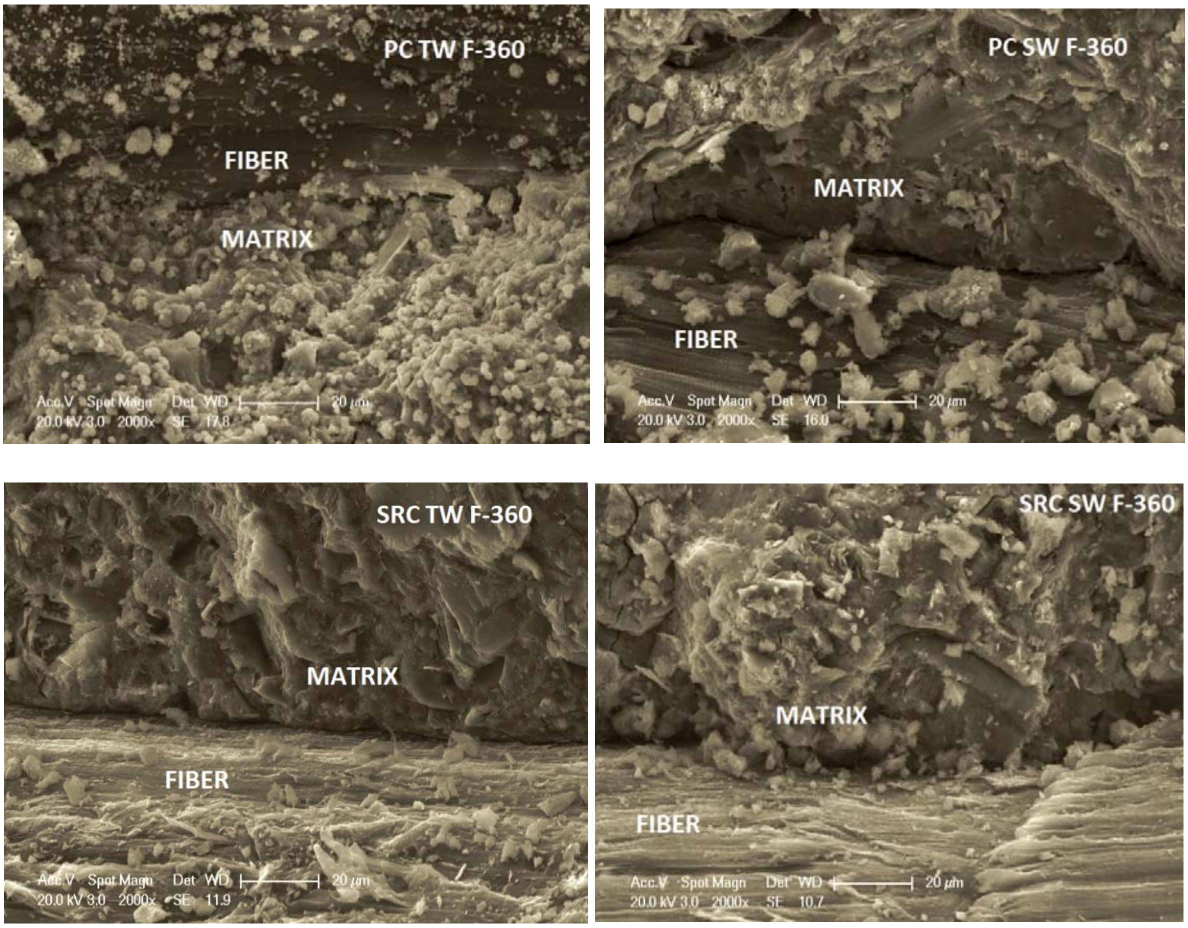


Figure 3.6. SEM pictures (cont.)

For most of the pictures in Figure 3.6, the difference between fiber surface and matrix surface could not be distinguished clearly. It was seen that fiber-matrix adherence was good enough.

However, according to Figure 3.7, it was seen that the adherence between the fibers and the matrix was different for seawater and tap water concrete. The polymer fibers used in this study had some factory made notches on them. The SEM micrographs showed that almost all of the notches on the fibers were filled with cement matrix when tap water was used representing very good adherence between the matrix and the fibers. Blue circles showed filled notches by cement matrix and red circles showed empty notches. The toughness difference mentioned in

Section 3.2.1.3 was considered to result from this. On the other hand, seawater Portland cement concrete samples did not show good improvement to fill notches from early ages to 360th day (from b to f). Nonetheless, seawater SRC concrete samples showed good development to fill notches from 28th day to 360th day (from d to h). As it was mentioned in Section 3.2.1.3, the toughness difference between tap water and seawater concrete diminished, especially for SRC concrete. More filled notches in seawater SRC concrete decreased the toughness difference more. It is also planned to examine the adherence by conducting direct tensile tests for the future studies.

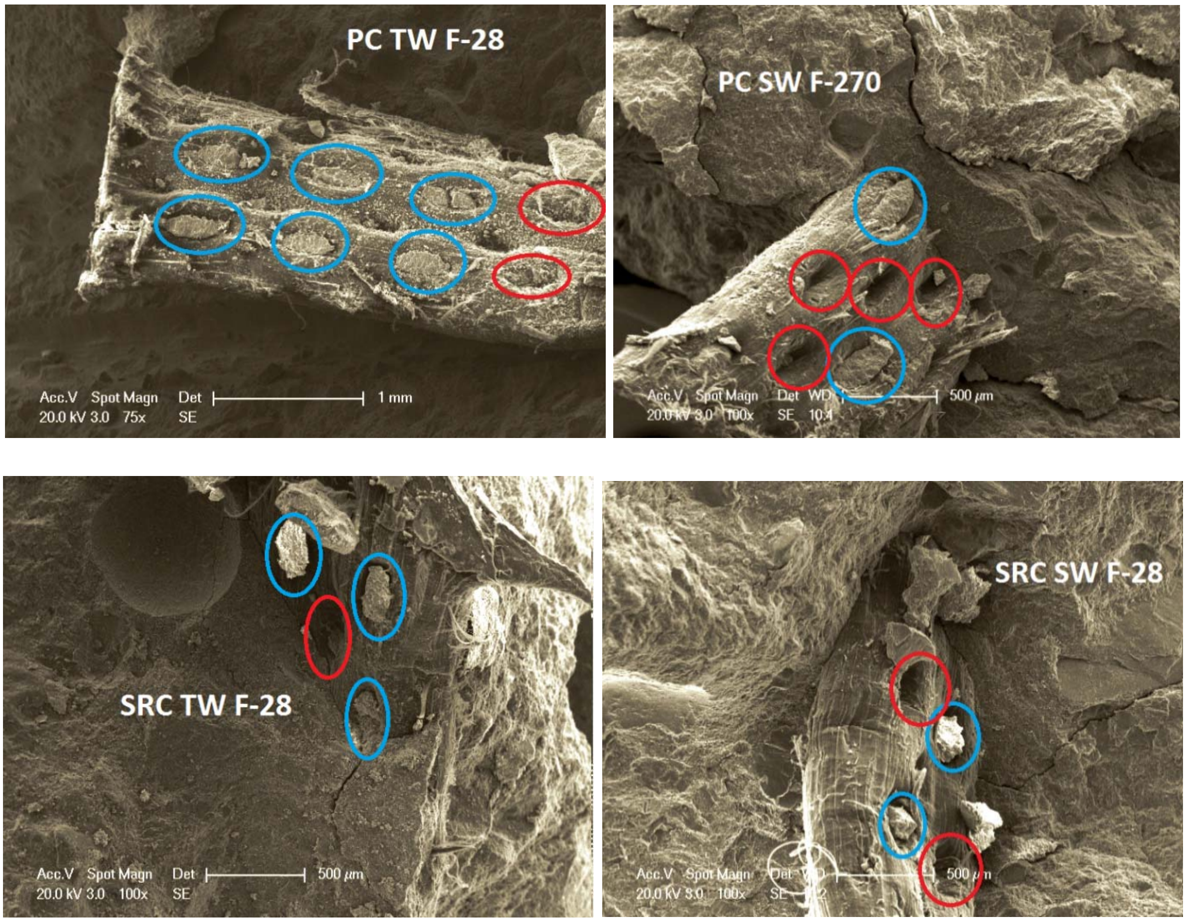


Figure 3.7. SEM pictures of the notches

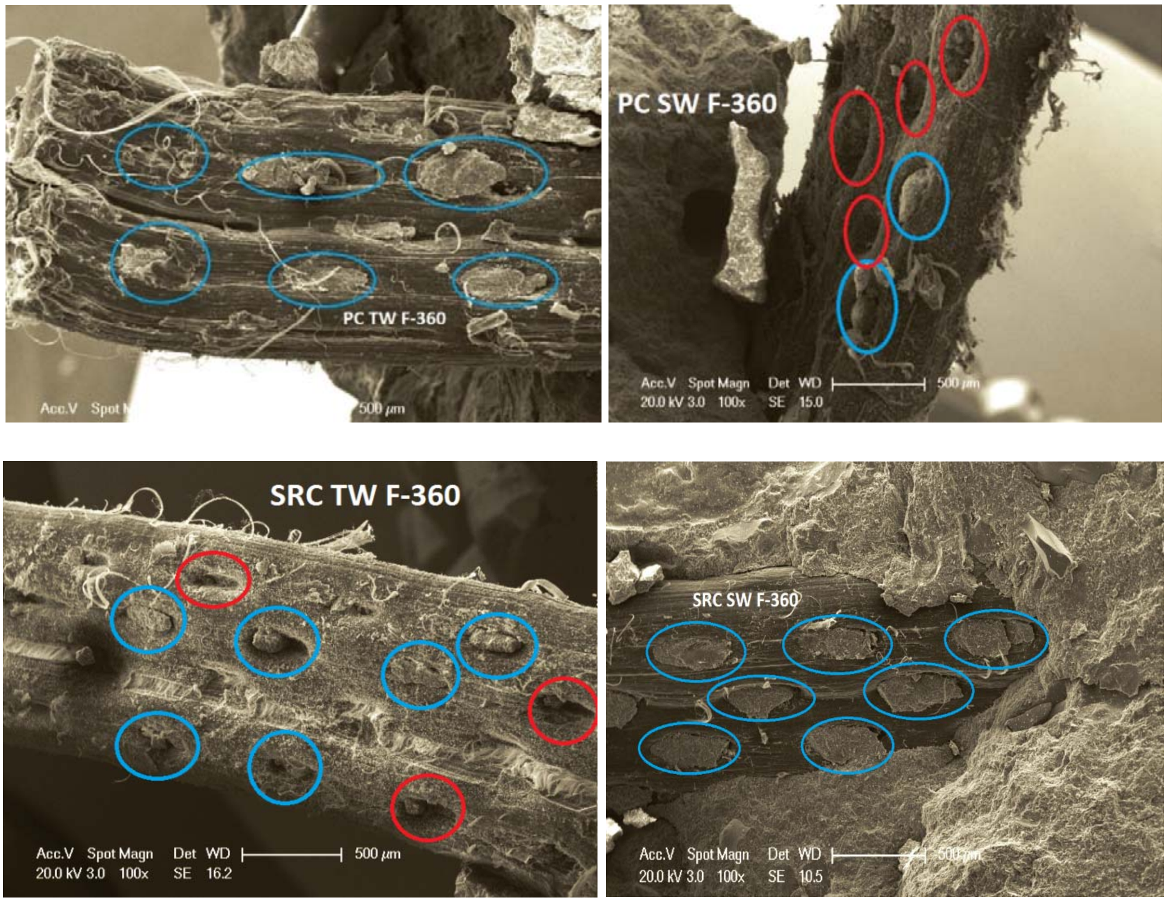


Figure 3.7. SEM pictures of the notches (cont.)

<u>3.2.2.12. XRD Analysis.</u> The samples for XRD analyzes were taken from the center and the surface of the fiber-free specimens. XRD analyzes were performed on the samples at 28th, 270th and 360th days. The investigated minerals' names, abbreviations and PDF-numbers were shown in Table 3.4. Gypsum was not observed for all concrete types at any ages. Therefore, it was not shown in the graphical results. Clinochlore, Muscovite and Quartz mineral came from the aggregates (Figure 2.2).

Table 3.4. Investigated minerals

Abbreviations	**Minerals**	**Compositions**	**PDF Numbers**
-	Gypsum	$CaSO_4.2H_2O$	33-0311
E	Ettringite	$Ca_6Al_2(SO_4)_3(OH)12.26H_2O$	41-1451
P	Portlandite	$Ca(OH)_2$	04-0733
Clino	Clinochlore	$Fe_6(Si,Al)_4O_{10}(OH)_8$	29-0701
A	Anhydrate	$CaSO_4$	86-2270
F	Friedel's salt	$3CaO.Al_2O_3.CaCl_2.10H_2O$	-
Q	Quartz	SiO_2	85-0795
Muscovite	Muscovite	-	76-0668

Time dependent results were given for all concrete types. For each of the compounds, the first peaks represented the characteristic peak (i.e. 1E) while the second peak addressed the second highest (i.e. 2E).

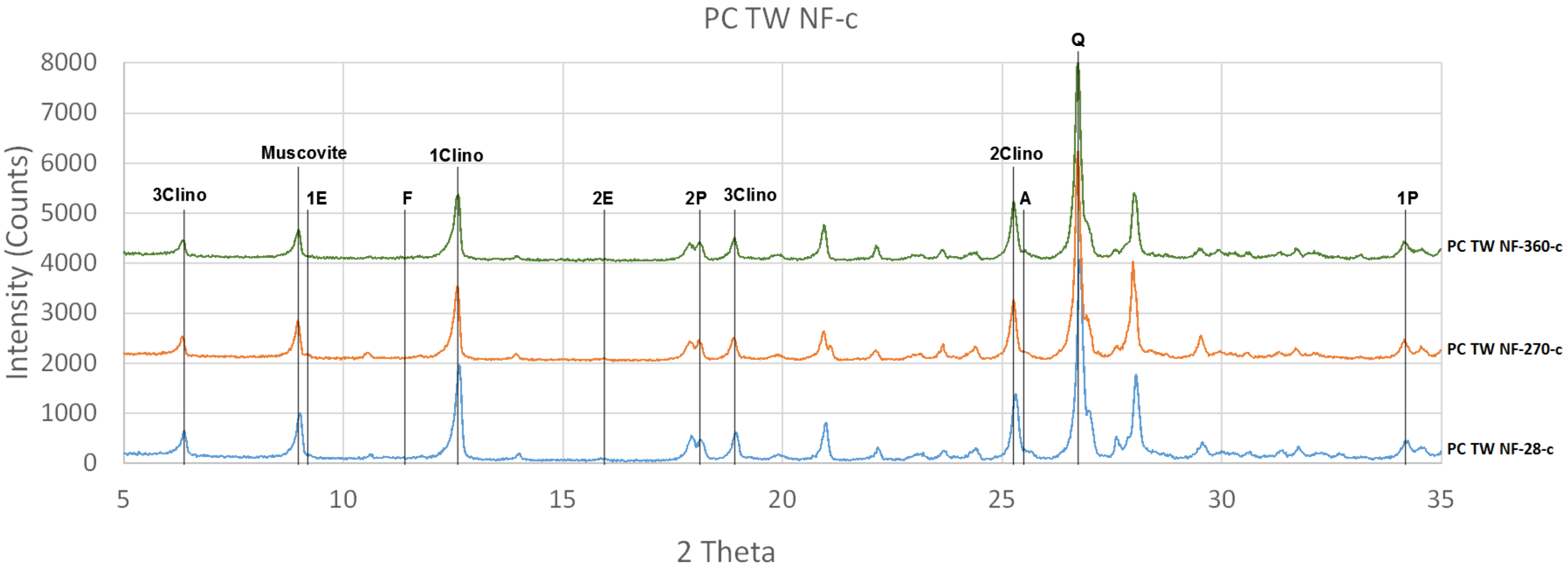


Figure 3.8. Time dependent results of PC TW NF-center

According to Figure 3.8, the peaks of ettringite crystals were not high. The intensity of ettringite and anhydrate ($CaSO_4$) crystals were similar for all ages. There were not a meaningful difference over time. Furthermore, the minimum portlandite content was detected at 360 day. The details of portlandite peaks could be seen in Figure 3.9. The reason for this can be explained as follows: Even though hydration reactions continued and $Ca(OH)_2$ crystals were generated, the rate of the reactions decreased day by day. In addition, more $Ca(OH)_2$ crystals were consumed to form $CaCO_3$. Friedel's salt was not detected for all ages due to the low amount of chloride ions in tap water.

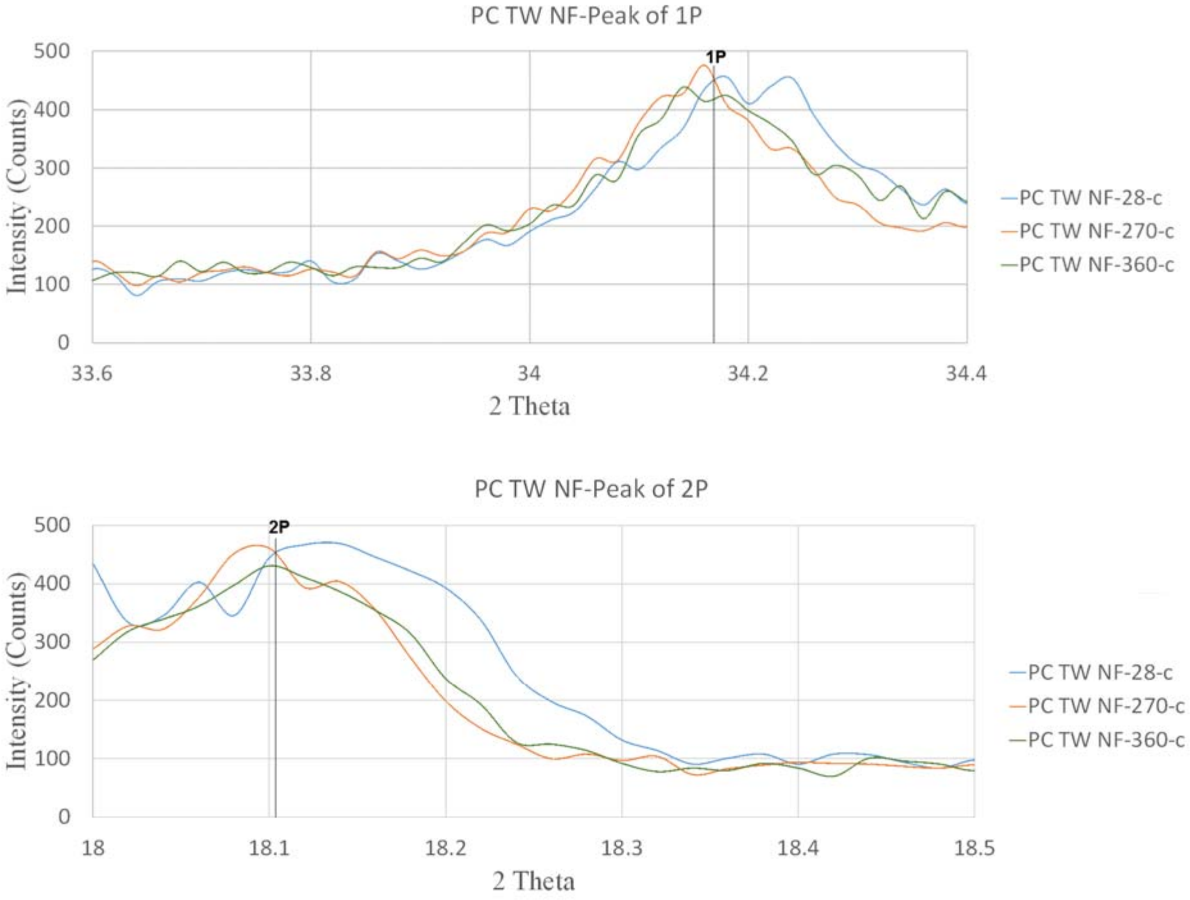


Figure 3.9. Details of portlandite's peaks of PC TW NF

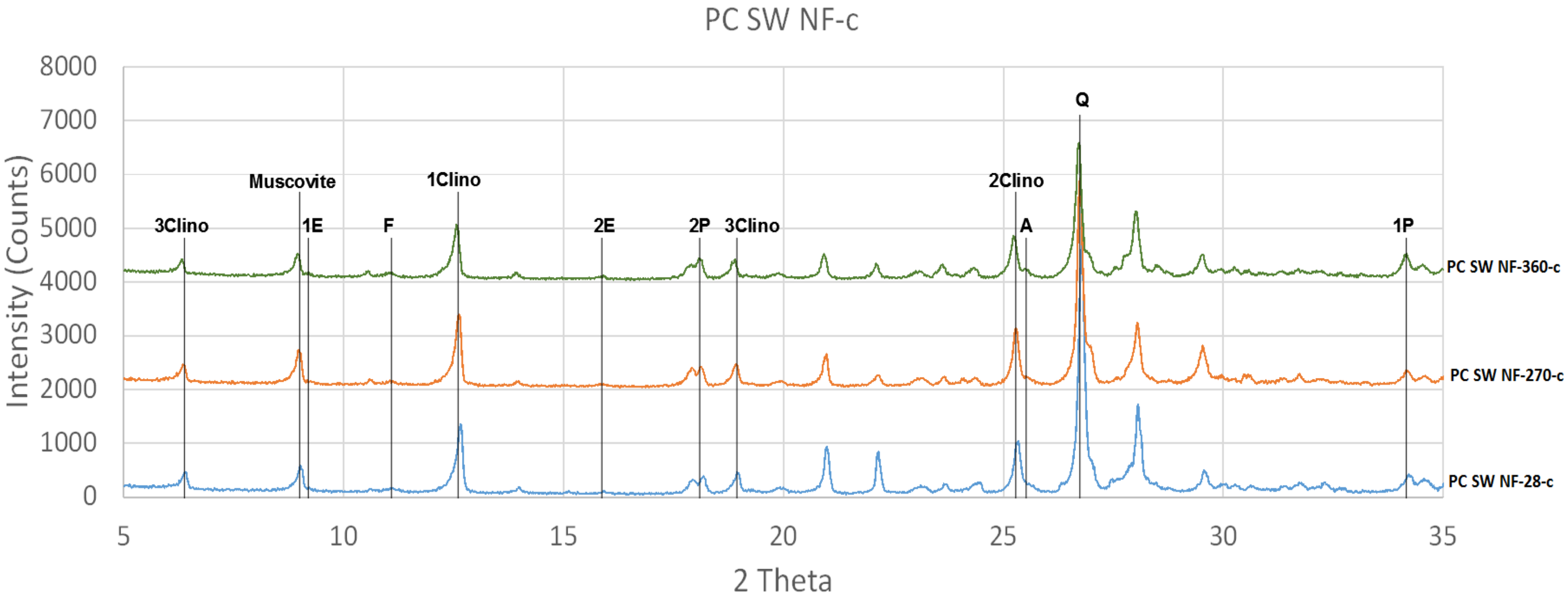


Figure 3.10. Time dependent results of PC SW NF-center

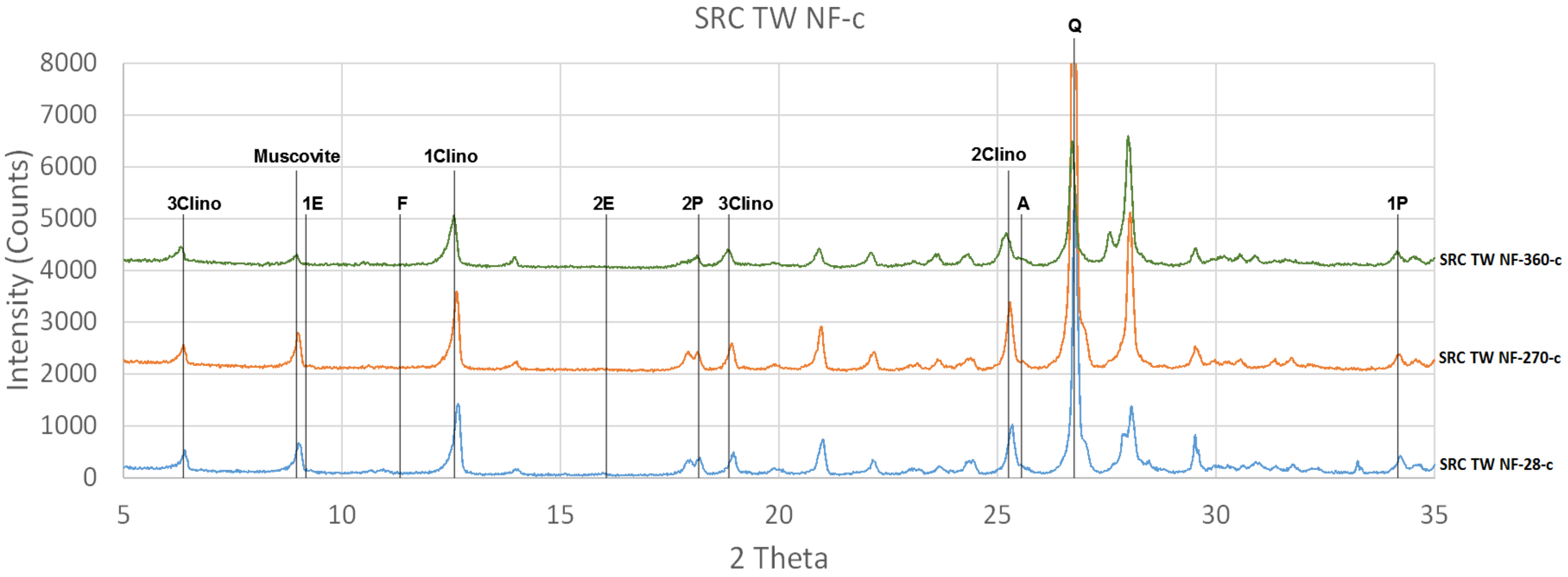


Figure 3.11. Time dependent results of SRC TW NF-center

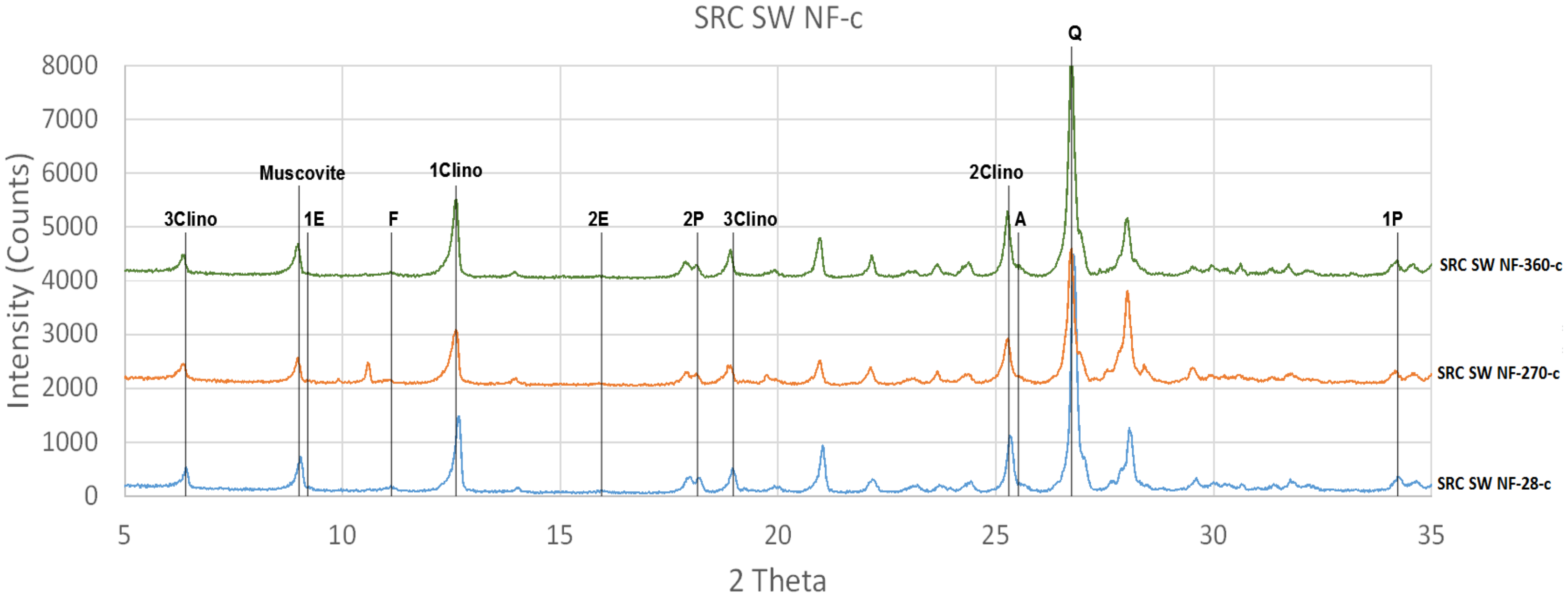


Figure 3.12. Time dependent results of SRC SW NF-center

Figure 3.10 showed the XRD analyses results for PC SW NF center. According to Figure 3.10, even though there were high amounts of sulfate ions in the mix water, the peaks of ettringite crystals were not high. The intensity of ettringite and anhydrate ($CaSO_4$) crystals were similar for all ages, likewise the results of PC TW NF-c. The intensity of portlandite crystals was similar at 28 day and 270 day; however, it was relatively higher at 360 day than before. Friedel’s salt formation was observed at all ages because of the chloride content of seawater. The intensity of FS formation was similar for all ages.

Figure 3.11 showed the XRD analyses results for SRC TW NF center. According to the figure, the intensity of ettringite crystals was not high. The intensity of ettringite and anhydrate crystals did not change significantly over time. The minimum portlandite content was detected at 360 day as a result of pozzolonic and carbonation reactions in SRC matrix. FS was not observed because of the low amount of chloride ions in tap water.

Figure 3.12 showed the XRD analyses results for SRC SW NF center. According to Figure 3.12, the intensity of ettringite and anhydrate crystals did not change significantly over time. The maximum portlandite content was detected at 28 day and decreased over time due to pozzolonic and carbonation reactions. The contribution of FS formation on the consumption of portlandite crystals was probably not pronounced after 28 days since the intensity of FS was similar for all ages.

In summary:

- Even though the amount of sulfate ions in seawater was very high, the intensity of ettringite crystals was not found to be high since C_3A and/or its products were bound by chloride ions to form FS [10]. Moreover, meaningful changes were not observed on the intensity of anhydrate and ettringite crystals over time for both seawater and tap water concrete.

- Portlandite content decreased over time due to carbonation and pozzolonic reactions (valid for SRC). The contribution of FS formation on the consumption of portlandite crystals in the seawater concrete as a result of Equation 1.1, Equation 1.2 and Equation 1.6 was not considered important after 28 days since the intensity of FS was similar for all ages.
- FS was observed only in seawater concrete samples due to the high amounts of chloride ions in seawater as expected. The most important part of FS was produced until 28 day. After 28 days, the intensity of FS did not change significantly.

According to XRD data, two different comparisons were performed; mixing water comparison and binder comparison. The all graphical results of mix water comparison and binder comparison were shown in Appendix A and Appendix B, respectively.

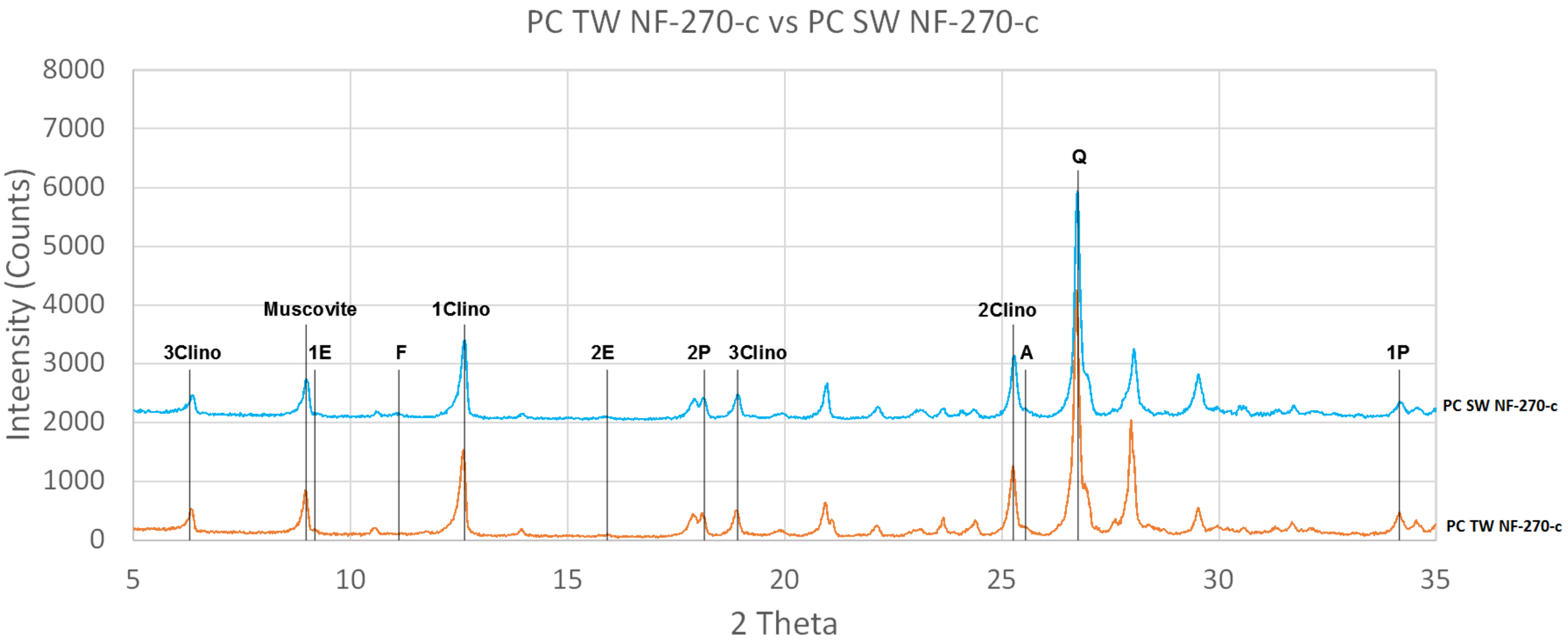


Figure 3.13. PC TW NF-270-c vs PC SW NF-270-c

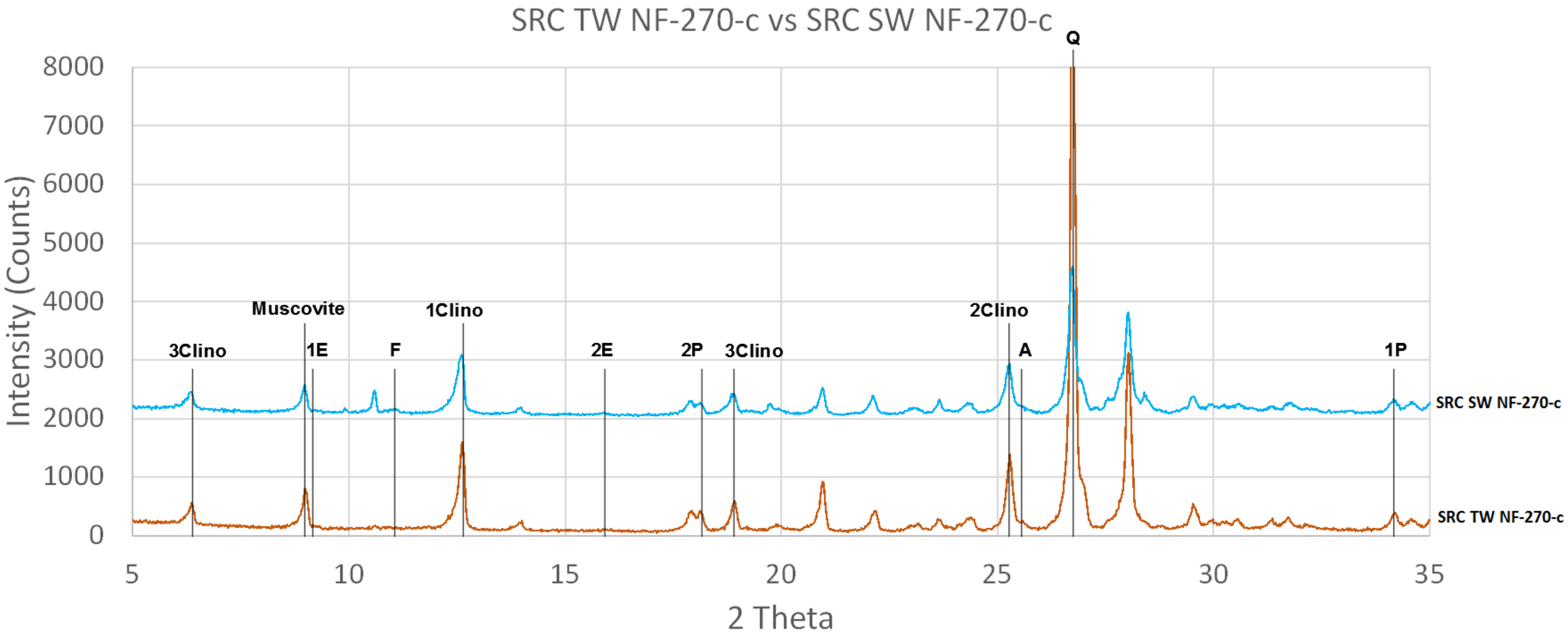


Figure 3.14. SRC TW NF-270-c vs SRC SW NF-270-c

According to Figure 3.13 and Figure 3.14, though higher sulfate concentration in the seawater, the intensity of ettringite and anhydrate crystals were found to be similar at the end of 9 months for both seawater and tap water concrete. The intensity of portlandite crystals was lower in seawater concrete samples due to the consumption of portlandite to form Friedel's salt [10] and $CaCl_2$ [4], [10]. FS formation was detected only in the seawater concrete samples because of chloride content in seawater.

A table was prepared to compare the hydration products for different types of mixing water based on the data given Appendix A. In the Appendix A, the graphical XRD results of the comparison of seawater and tap water concrete samples from 28th day to 360th were shown.

Table 3.5. The comparison of hydration products for different types of mixing water

Samples Codes	**Portlandite**	**Ettringite**	**Gypsum**	**Anhydrate**	**Friedel's Salt**
PC NF-28-c	Tap Water	Similar	Not Found	Similar	Seawater
PC NF 28-s	Seawater	Similar	Not Found	Similar	Seawater
PC NF-270-c	Tap Water	Similar	Not Found	Similar	Seawater
PC NF-270-s	Tap Water	Similar	Not Found	Similar	Seawater
PC NF-360-c	Similar	Similar	Not Found	Similar	Seawater
PC NF-360-s	Tap Water	Similar	Not Found	Similar	Seawater
SRC NF-28-c	Tap Water	Similar	Not Found	Similar	Seawater
SRC NF 28-s	Similar	Similar	Not Found	Similar	Seawater
SRC NF-270-c	Tap Water	Similar	Not Found	Similar	Seawater
SRC NF 270-s	Tap Water	Similar	Not Found	Similar	Seawater
SRC NF-360-c	Similar	Similar	Not Found	Seawater	Seawater
SRC NF 360-s	Tap Water	Similar	Not Found	Similar	Seawater

The XRD results can be categorized as;

- *Ettringite, Gypsum, Anhydrate*: Even though gypsum was present 5% in PC and SRC, it was not detected in all concrete samples at all ages according to XRD results. These crystals could be consumed to form ettringite crystals and could be transformed to anhydrate. Excessive sulfate ions in seawater did not lead to formation of gypsum because of consumption of $Ca(OH)_2$ to form $Ca(CO)_3$ and Friedel's salt [10]. Intensity of anhydrate were similar in all concrete samples at almost all ages. Like anhydrate results, ettringite crystals were similar for both tap water and seawater concrete samples. Even though seawater contained much more sulfate ions than tap water, the intensity of ettringite crystals were found to be similar. This result was attributed to depletion of C_3A and its products by formation of Friedel's salt [5]–[7], [9], [10], [17]–[19]. This effect mitigated further formation of ettringite crystals in seawater concrete. Decrease in mechanical strength because of the expansion due to the formation of anhydrate and/or ettringite crystals was not detected. This data was supported by mechanical test results of seawater and tap water concrete.

- *Portlandite*: The intensity of Portlandite crystals of tap water concrete was generally higher than that of seawater concrete. It could be attributed to formation of $CaCl_2$ by reaction of Portlandite and Cl^- ions [4], [10]. $CaCl_2$ is known as an accelerator. Although the results of compression test were similar, the formation of $CaCl_2$ affected the setting time. Seawater pastes showed shorter setting times than tap water pastes. Moreover, portlandite crystals were consumed to form Friedel's salt [10].

- *Friedel's Salt*: Friedel's salt, which binds chloride ions, were detected for all seawater concrete samples at all ages. However, it was not seen in tap water concrete samples as a result of low chloride content of tap water. The effect of excessive sulfate ions in seawater was minimized by depletion of C_3A and its products to formation of Friedel's salt [5]–[7], [9], [10], [17]–[19].

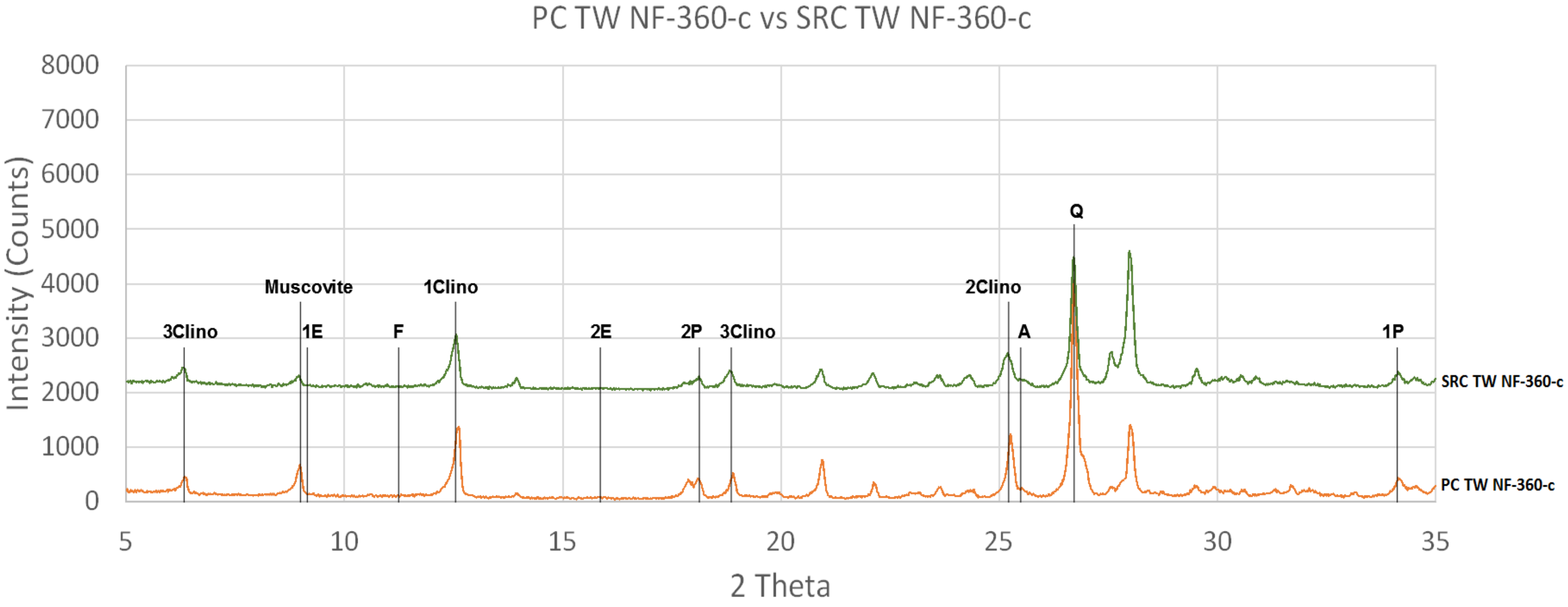


Figure 3.15. PC TW NF-360-c vs SRC TW NF-360-c

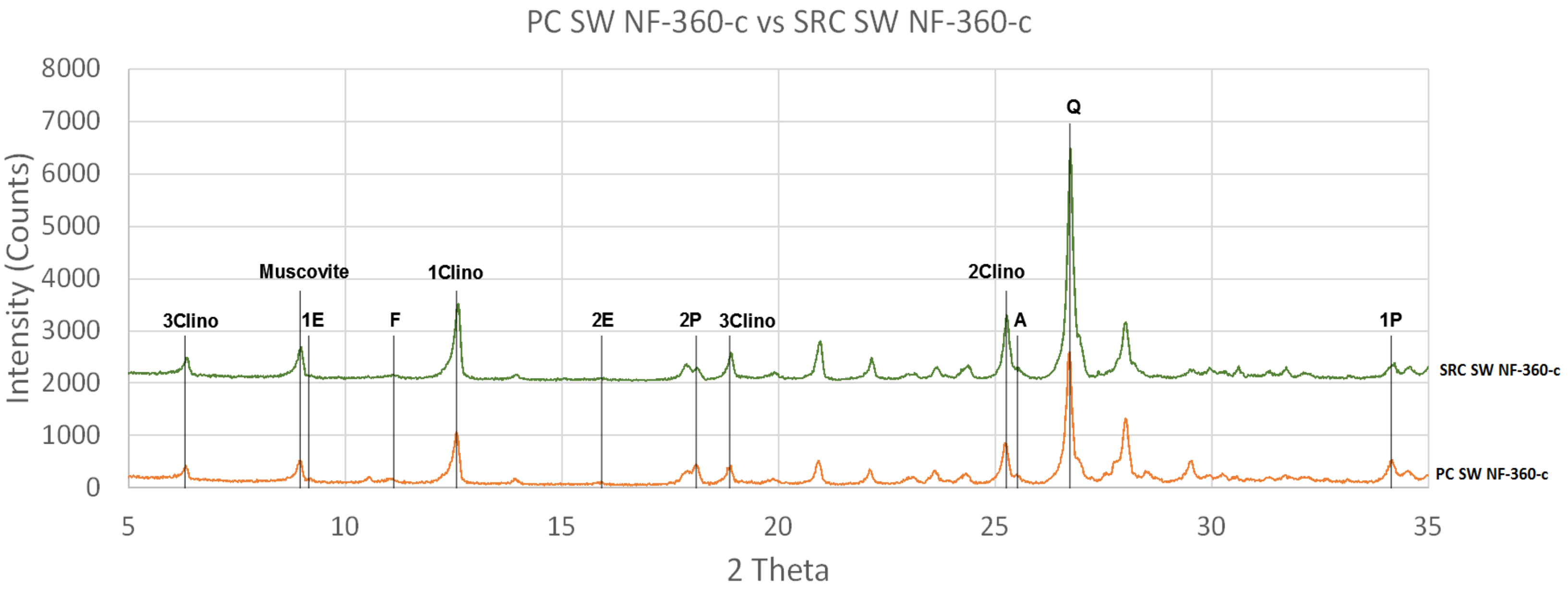


Figure 3.16. PC SW NF-360-c vs SRC SW NF-360-c

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According to Figure 3.15, the intensity of ettringite and anhydrate crystals were found to be similar at the end of 12 months. The intensity of portlandite crystals was found to be lower in SRC concrete because of pozzolonic reactions. Friedel’s salt formation was not observed for both concrete samples as a result of low chloride content in the mix water.

According to Figure 3.16, the intensity of ettringite crystals was found to be similar. Even though the intensity of anhydrate was similar for PC and SRC concrete at all ages (except this one (360-c)), the intensity of anhydrate was relatively higher in SRC concrete sample at 360 day. The intensity of portlandite crystals was found to be lower in SRC concrete because of pozzolonic reactions. FS formation was detected for both concrete samples. The intensity was similar.

A table was prepared to compare the hydration products for different binder materials by using the data given Appendix B. In the Appendix B, the graphical XRD results of the comparison of PC and SRC concrete samples from 28th day to 360th day were shown

Table 3.6. The comparison of hydration products for different types of binder materials

Samples Codes	**Portlandite**	**Ettringite**	**Gypsum**	**Anhydrate**	**Friedel’s Salt**
TW NF-28-c	PC	Similar	Not Found	Similar	Not Found
TW NF-28-s	Similar	Similar	Not Found	Similar	Not Found
TW NF-270-c	PC	Similar	Not Found	Similar	Not Found
TW NF-270-s	PC	Similar	Not Found	Similar	Not Found
TW NF-360-c	PC	Similar	Not Found	Similar	Not Found
TW NF-360-s	PC	Similar	Not Found	PC	Not Found
SW NF-28-c	PC	Similar	Not Found	Similar	Similar
SW NF-28-s	PC	Similar	Not Found	Similar	Similar
SW NF-270-c	PC	Similar	Not Found	Similar	Similar
SW NF-270-s	PC	Similar	Not Found	Similar	Similar
SW NF-360-c	PC	Similar	Not Found	SRC	Similar
SW NF-260-s	Similar	Similar	Not Found	Similar	SRC

- *Ettringite, Gypsum, Anhydrate*: Gypsum crystals were not detected in all concrete samples at all ages. These crystals could be consumed to form ettringite crystals and could be transformed to anhydrate. Intensity of anhydrate crystals were similar in all concrete samples at almost all ages. Like anhydrate results, the intensity of ettringite crystals were similar for both Portland cement and SRC concrete samples.

- *Portlandite*: The content of portlandite was detected higher in PC concrete than SRC concrete for almost all samples as expected. Secondary (pozzolonic) reactions was occurred in SRC concrete samples and these reactions consumed portlandite crystals.

- *Friedel's Salt*: It was detected in only seawater concrete samples due to the presence of excessive chloride ions. The Friedel's salt content was similar for PC and SRC concrete almost at all ages. Even though more alumina content in SRC promoted the formation of FS [5]–[7], [10] as a result of Equation 1.6, less C_3A content in SRC did not support the formation of FS as a result of Equation 1.1, Equation 1.2, Equation 1.3, Equation 1.4 and Equation 1.5. Therefore, the different alumina content of PC and SRC (Table 2.1) might not be enough to produce more FS in SRC concrete.

4. CONCLUSIONS

Fresh water is the source of life for any kinds of living creature. As a result of unsustainable usage of fresh water by humanity, water scarcity increases day by day. In addition to use it as drinking water, it is used in many sectors; agriculture industry, textile industry, metallurgical industry, food industry etc. Construction industry is a sector that huge amount of fresh water is used for production concrete, cleaning, curing etc. Therefore, this sector contributes to the water shortages. The aim of this study is the use of seawater as mixing water in concrete rather than fresh water with a sustainable perspective to decrease the negative effect of construction industry on the water scarcity.

This topic has been investigated for some decades. However, the number of studies are very limited and when the research studies are examined, it can be seen that most of them focused on only mechanical effect of use of seawater as mixing water at early ages. However, as can be predicted, durability of concrete is very important for producing a sustainable material and durability is closely related to the microstructural changes occurring during the lifetime of the material. The presence of chloride and sulfate ions in seawater especially is expected to affect the microstructure and/or durability when compared to tap water concrete. This study is a part of a 2.5 years long project and in this part of the study the results of the 1st year were given. Detailed microstructural analyses were carried out to understand and evaluate the reasons for changes in the material behavior when seawater was used as the mix water for concrete. Two different binders (OPC and SRC) were used. Macro synthetic structural fibers were also utilized to see the effectiveness of these fibers when combined with seawater mixed concrete. The results can be summarized as follows;

- The use of seawater as the mix water for concrete did not have a negative effect on the strength of concrete up to one year. Compressive strength results of the seawater concrete and tap water concrete samples were similar. The early strength (at 7th day) of the samples produced by sulfate resistant cement was relatively low compared to the samples produced by OPC most probably due to slower reactions. However, this difference was closed up to 180th day and final strength of SRC concrete was relatively higher because of the pozzolanic reactions.

- The type of mixing water did not affect the elastic modulus results significantly for all ages. There was no significant difference between the elastic modulus of the samples produced by seawater and the samples produced by tap water up to the first 12 months. At the same time, the cement type had no significant effect on the modulus of elasticity. The elastic modulus development of the samples was similar.

- Fiber addition did not affect the compressive strength and elastic modulus results significantly.

- Flexural strength of seawater concrete was slightly higher than tap water at early ages; however, the strength was similar at the end of 1 year. Even though matrix-fiber adherence was good for both seawater and tap water concrete, the toughness values were decreased when seawater was used in fibrous concrete. SEM observations showed that tap water matrix filled the notches of fibers better. It is also planned to examine the adherence by conducting direct tensile tests in the future to understand the effect of seawater on the matrix-fiber adherence.

- Seawater contained much more sulfate and chloride ions when compared to tap water. The effects of these ions on the microstructure were investigated. Even though gypsum was present 5% in PC and SRC, it was not detected in all concrete samples at all ages according to XRD results. These crystals could be consumed to form ettringite crystals and could be transformed to anhydrate. Excessive sulfate ions in seawater did not lead to formation of gypsum because of consumption of $Ca(OH)_2$ to form $Ca(CO)_3$ and Friedel's salt as a consequence of Equation 1.1, Equation 1.2, and Equation 1.6.

- Even though seawater contained much more sulfate ions than tap water, the intensity of ettringite crystals were found to be similar for both tap water and seawater concrete samples. This result was attributed to depletion of C_3A and its products by formation of Friedel's salt. This effect mitigated further formation of ettringite crystals in seawater concrete.

- The intensity of Portlandite crystals of tap water concrete was generally higher than that of seawater concrete. It could be attributed to the formation of $CaCl_2$ by the reaction of Portlandite and Cl^- ions. $CaCl_2$ is known as an accelerator and that's why seawater decreased setting times. Moreover, portlandite crystals were consumed to form Friedel's salt in the seawater concrete samples.

- The content of portlandite was detected higher in PC concrete than SRC concrete for almost all samples as expected because of secondary reactions.

- Friedel's salt, which binds chloride ions, were detected for all seawater concrete samples at all ages. However, it was not seen in tap water concrete samples as a result of low chloride content of tap water. The effect of excessive sulfate ions in seawater was minimized by depletion of C_3A and its products to formation of Friedel's Salt. After 28th day, the intensity of FS did not change significantly.

- The Friedel's salt content was similar for PC and SRC concrete almost at all ages. Even though more alumina content in SRC promoted the formation of FS as a result of Equation 1.6, less C_3A content in SRC did not support the formation of FS as a result of Equation 1.1, Equation 1.2 and Equation 1.3, Equation 1.4 and Equation 1.5. Moreover, the different alumina contents of PC and SRC (Table 2.1) might not be enough to produce more FS in SRC concrete.

As it is mentioned, using seawater as the mix water for concrete is expected to decrease the use of fresh water in the concrete industry significantly. It can reduce the contribution effect of the concrete industry on water scarcity. Furthermore, some territories, such as islands, must transport fresh water. This transportation process can lead to more CO_2 emissions and it is expensive process. However, in these territories seawater can be obtained easily. The use of seawater as the mix water for concrete rather than tap water can decrease the CO_2 emissions and the cost of transportation in these territories.

Up to 1 year, results showed that seawater is a good option to be used as the mix water for concrete. Nevertheless, Friedel's salt formation and pH value of concrete should be observed because Friedel's salt is sensitive to pH changes[19]. If the pH is low enough, reversible reaction of Friedel's salt may occur and it returns to C_3A and its products. The reaming seawater in capillary pores, which is sulfate rich, can produce ettringite at hardened stage (Delayed Ettringite Formation) and damage the concrete.

In that study, the effect of the seawater as the mix water on the concrete properties were discussed. To purely understand the effect of the seawater on the microstructure of the paste, cement pastes will be produced and analyzed via XRD for the future study. The effects of seawater on the microstructure of cement paste and concrete will be compared.

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APPENDIX A: GRAPHICAL RESULTS OF MIX WATER COMPARISON

The graphical XRD results of the comparison of seawater and tap water concrete samples from 28th day to 360th were shown.

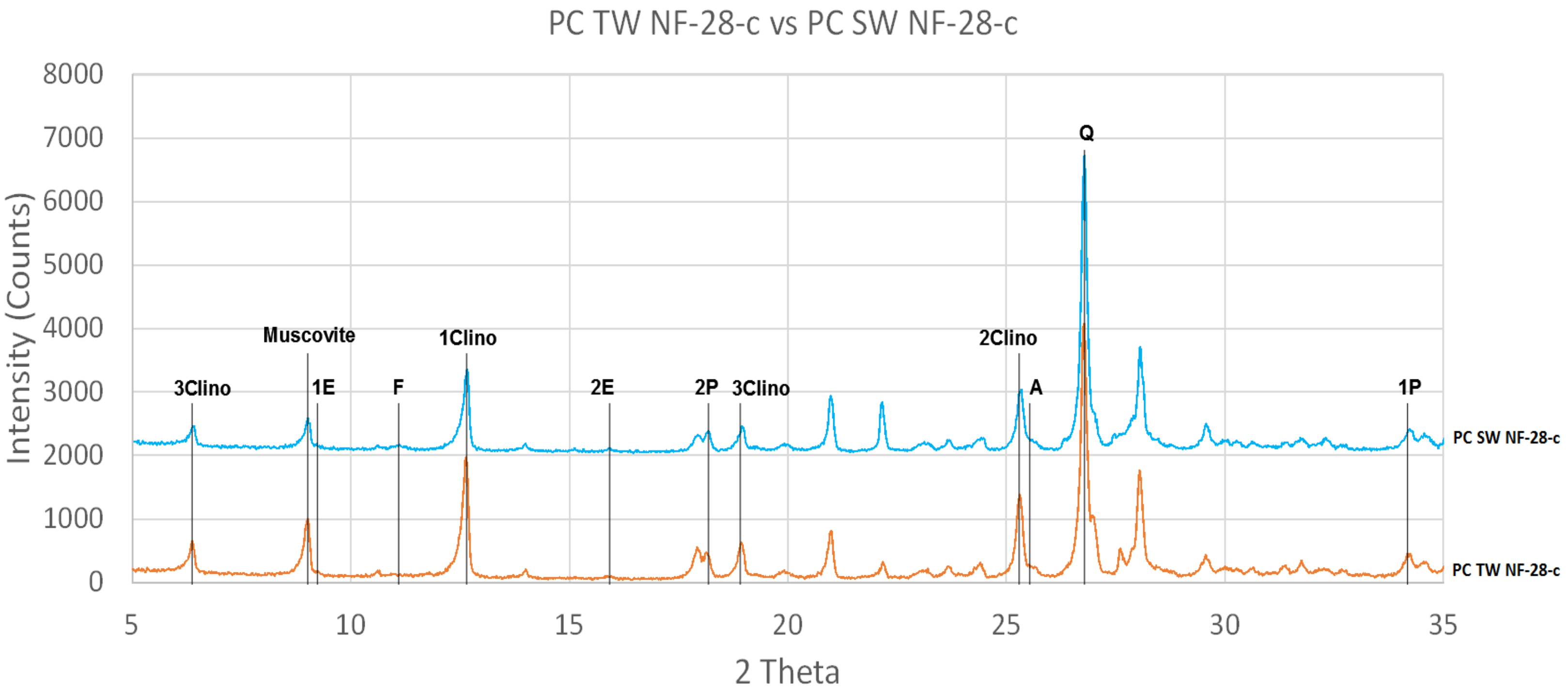


Figure A.1. PC TW NF-28-c vs PC SW NF-28-c

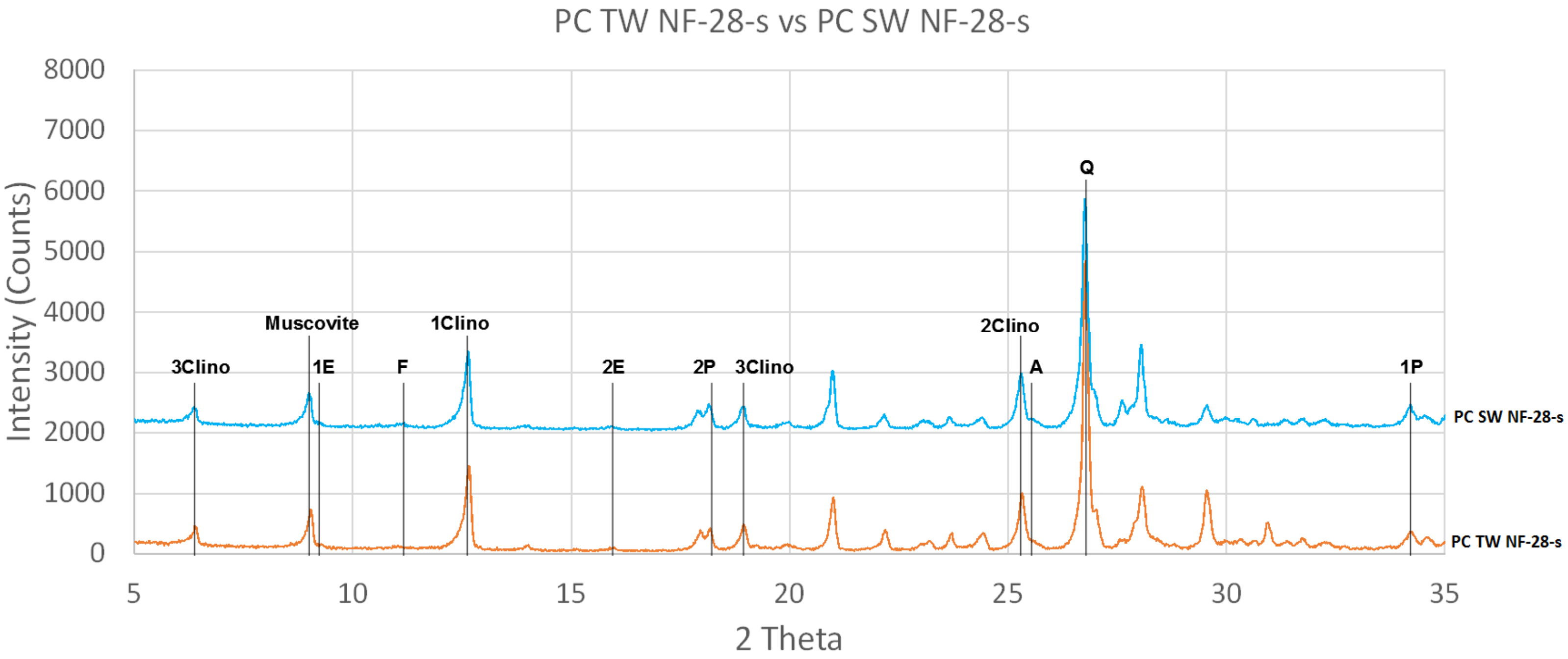


Figure A.2. PC TW NF-28-s vs PC SW NF-28-s

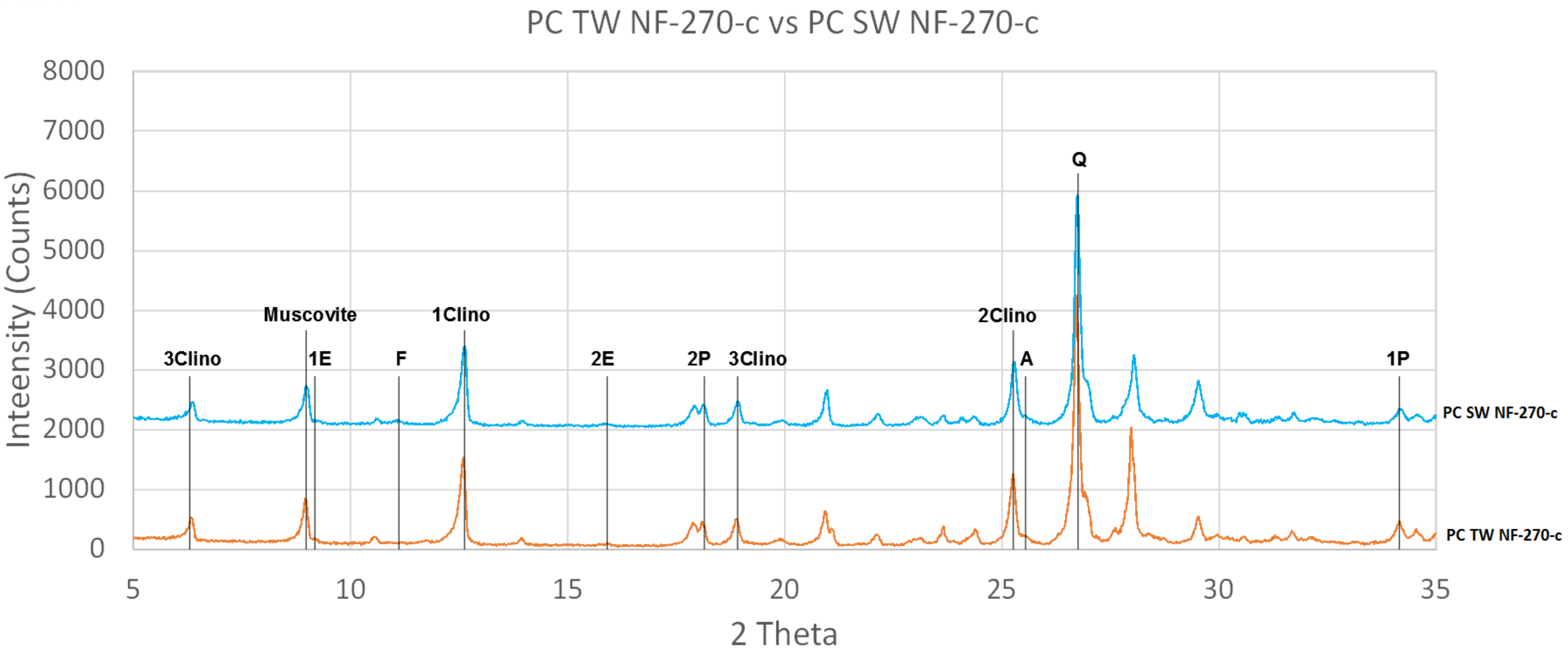


Figure A.3. PC TW NF-270-c vs PC SW NF-270-c

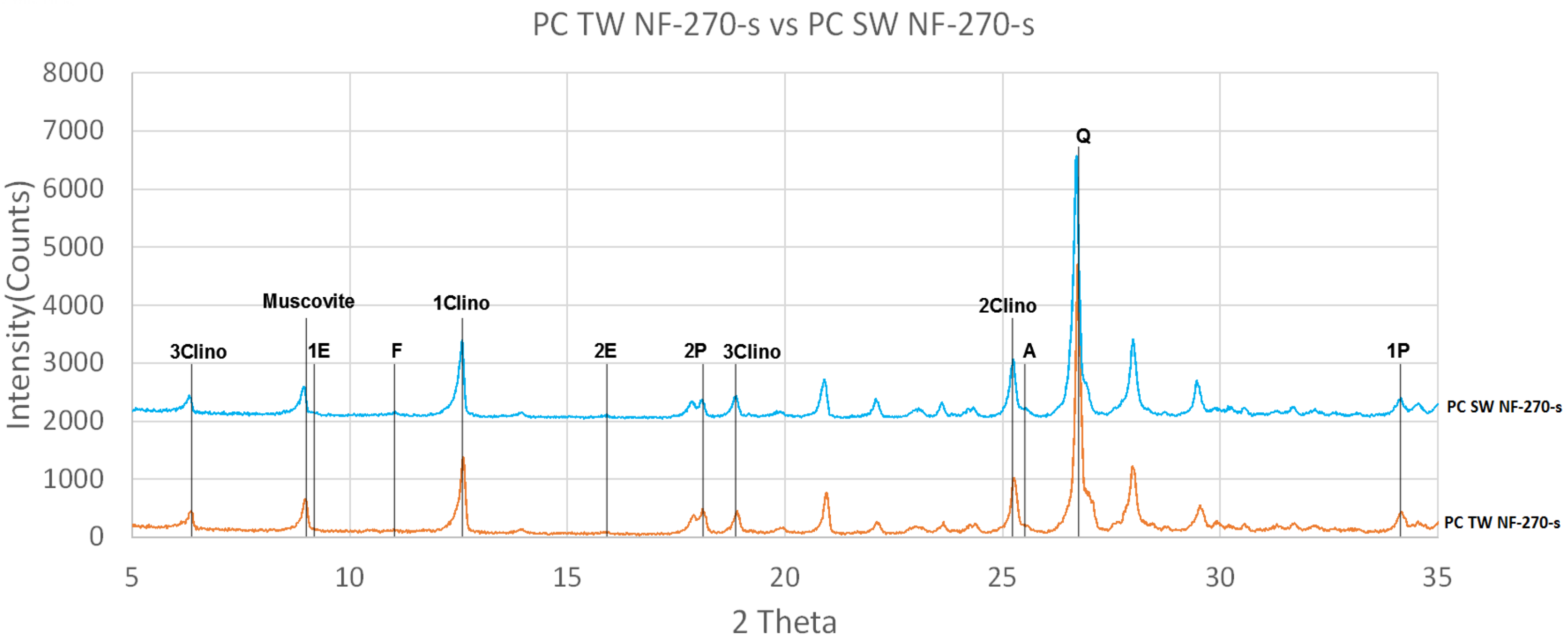


Figure A.4. PC TW NF-270-s vs PC SW NF-270-s

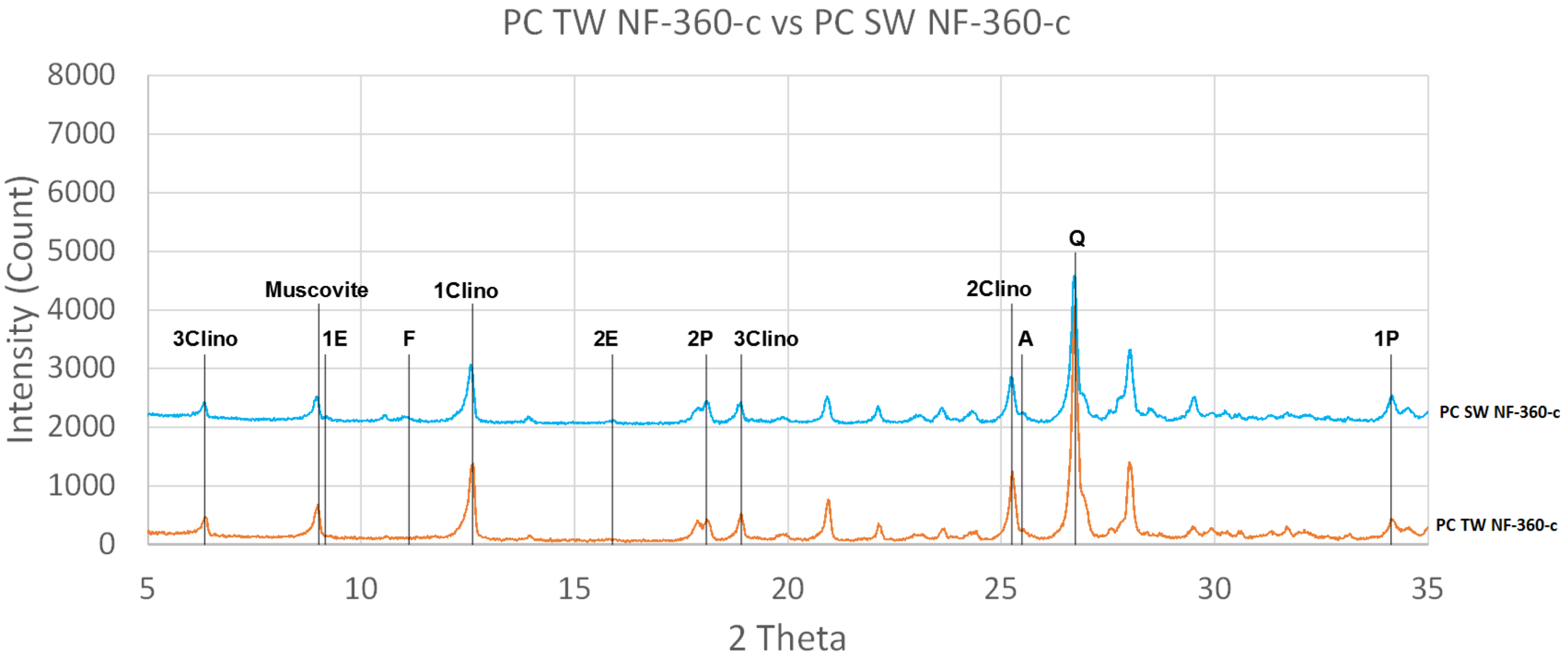


Figure A.5. PC TW NF-360-c vs PC SW NF-360-c

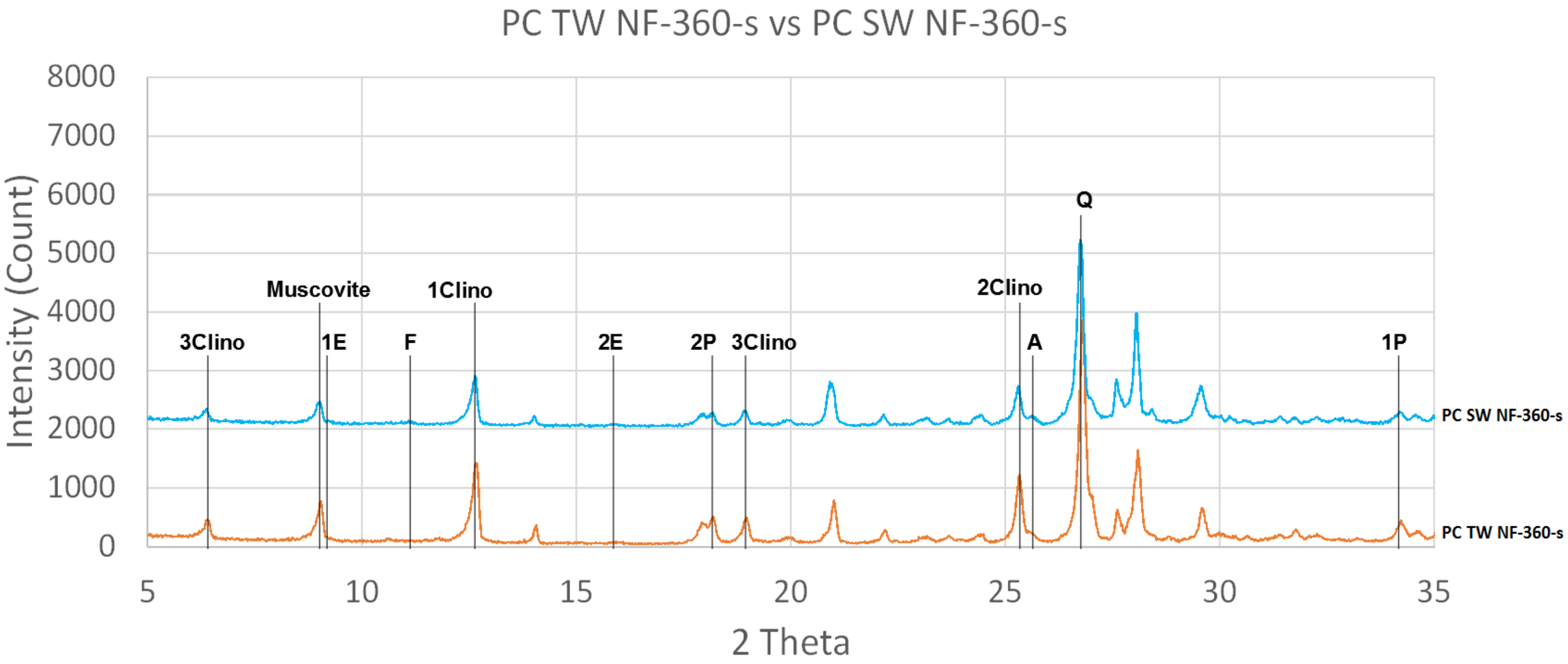


Figure A.6. PC TW NF-360-s vs PC SW NF-360-s

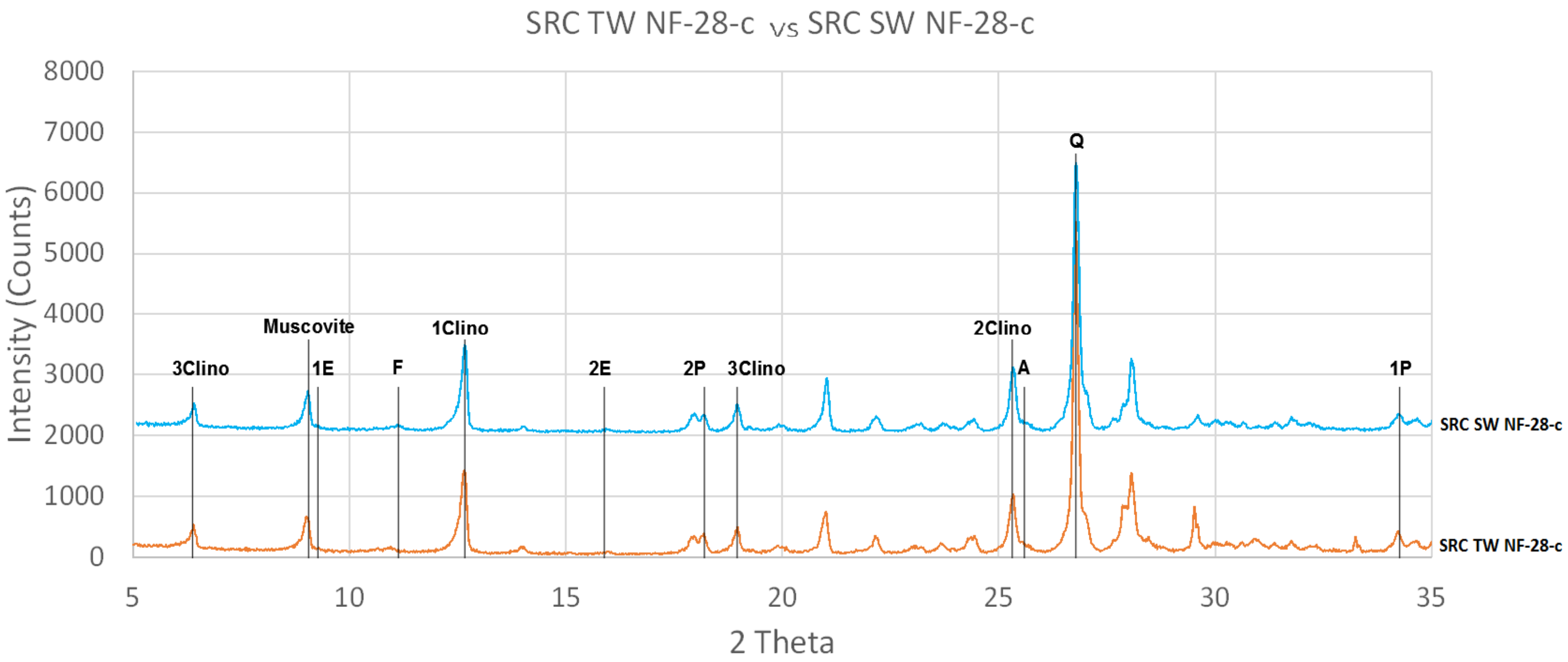


Figure A.7. SRC TW NF-28-c vs SRC SW NF-28-c

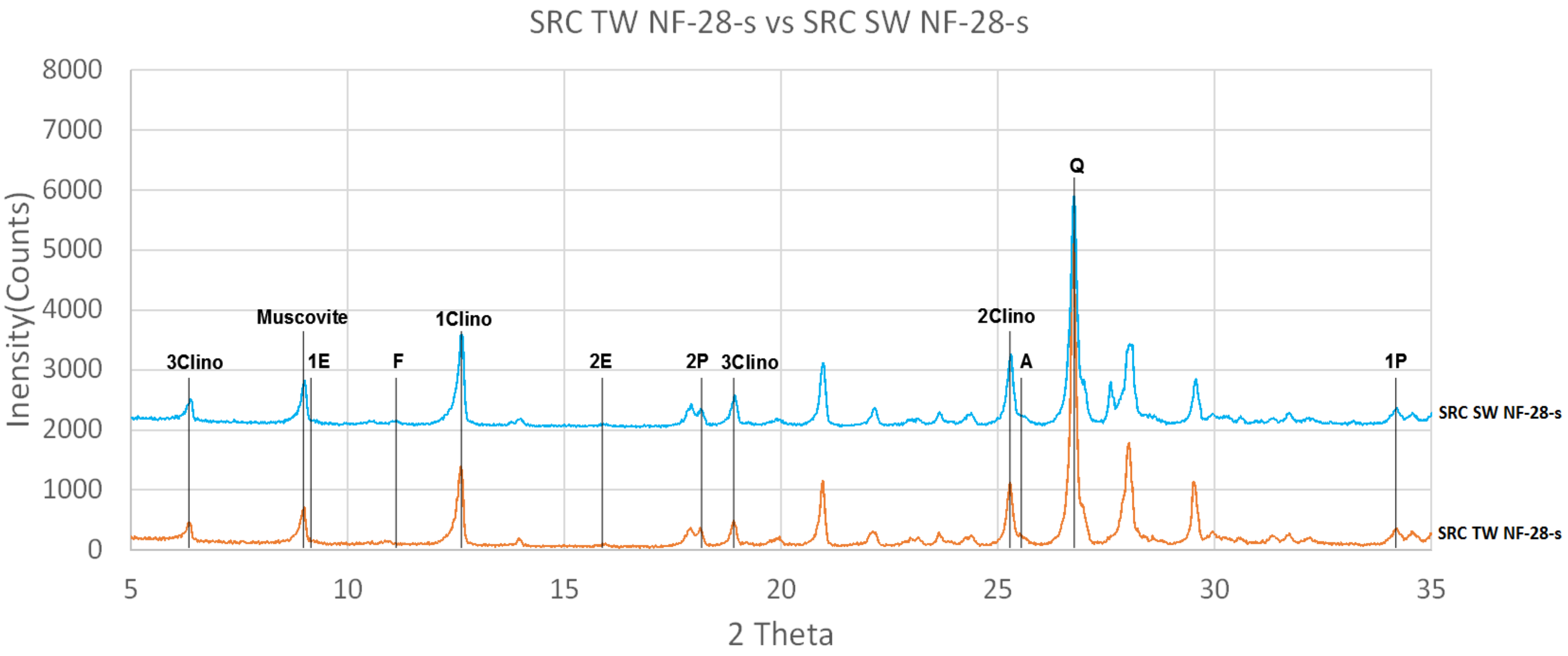


Figure A.8. SRC TW NF-28-s vs SRC SW NF-28-s

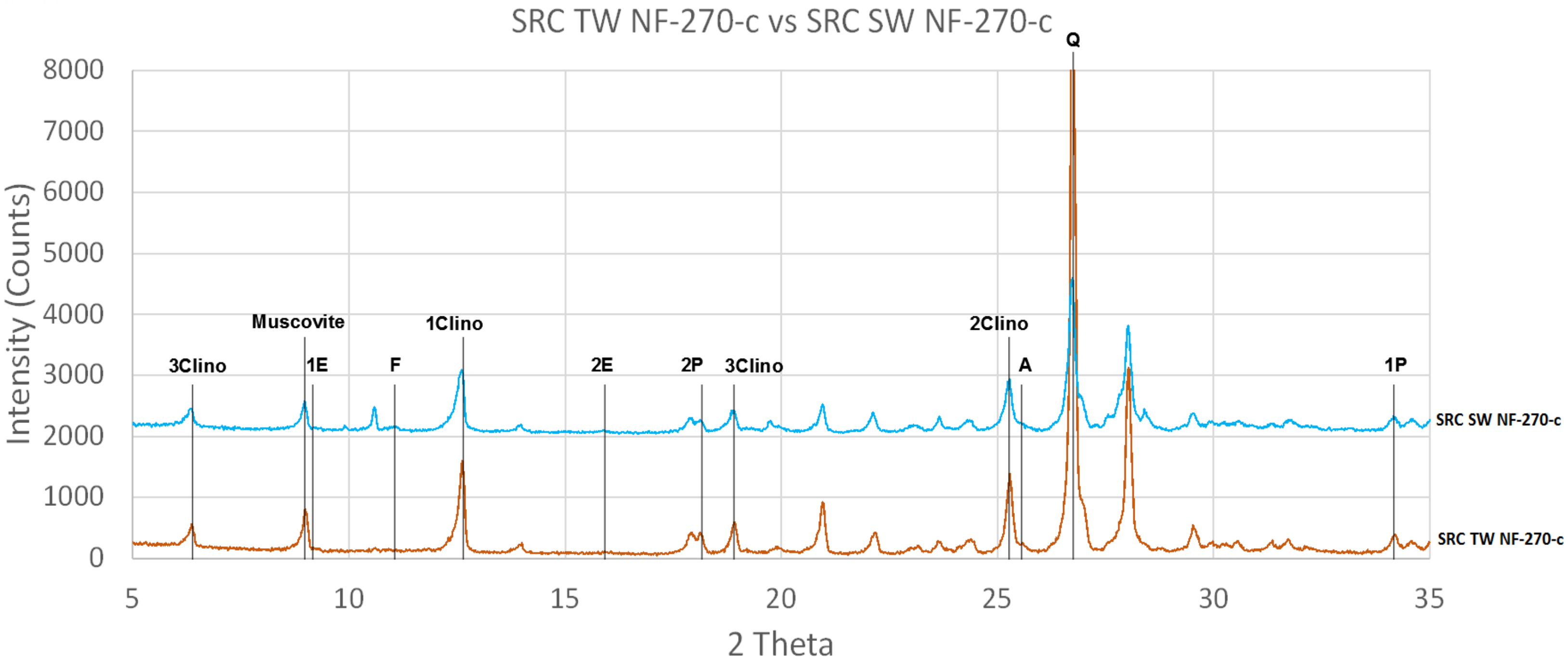


Figure A.9. SRC TW NF-270-c vs SRC SW NF-270-c

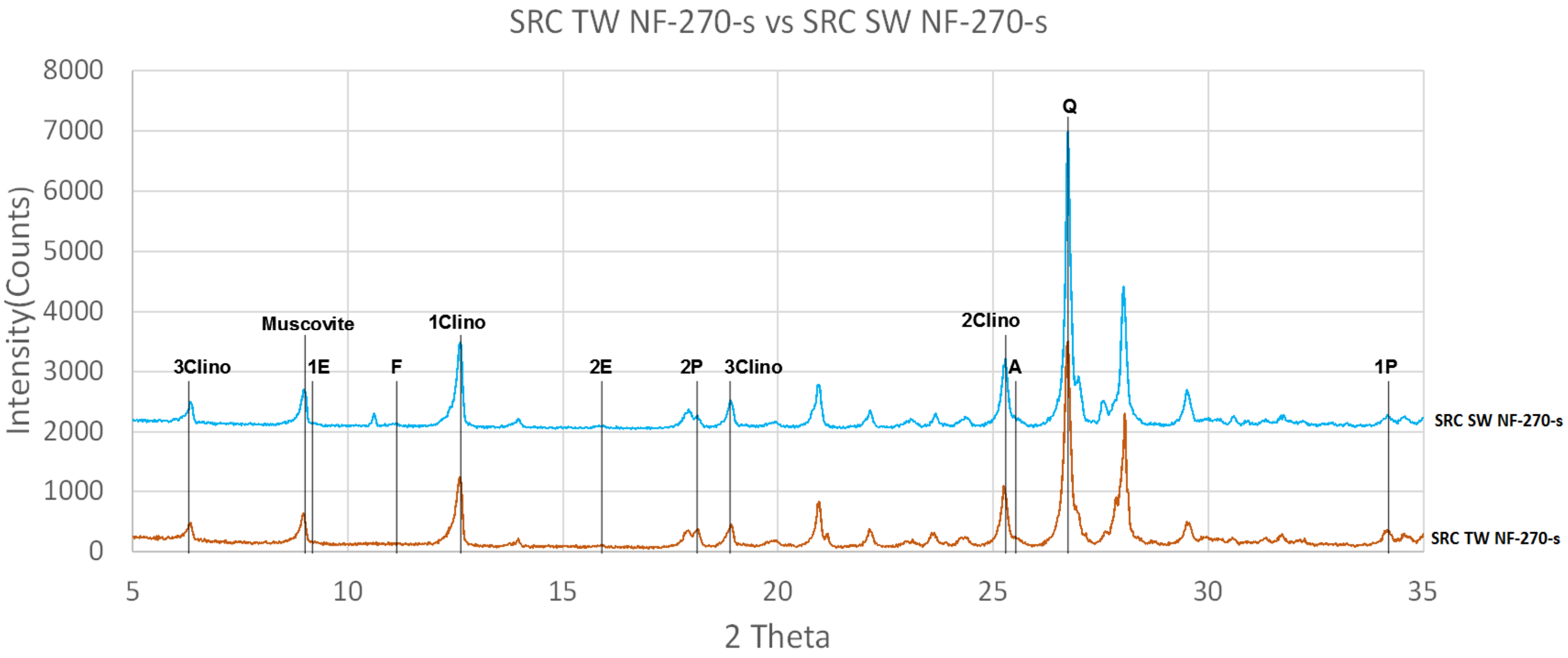
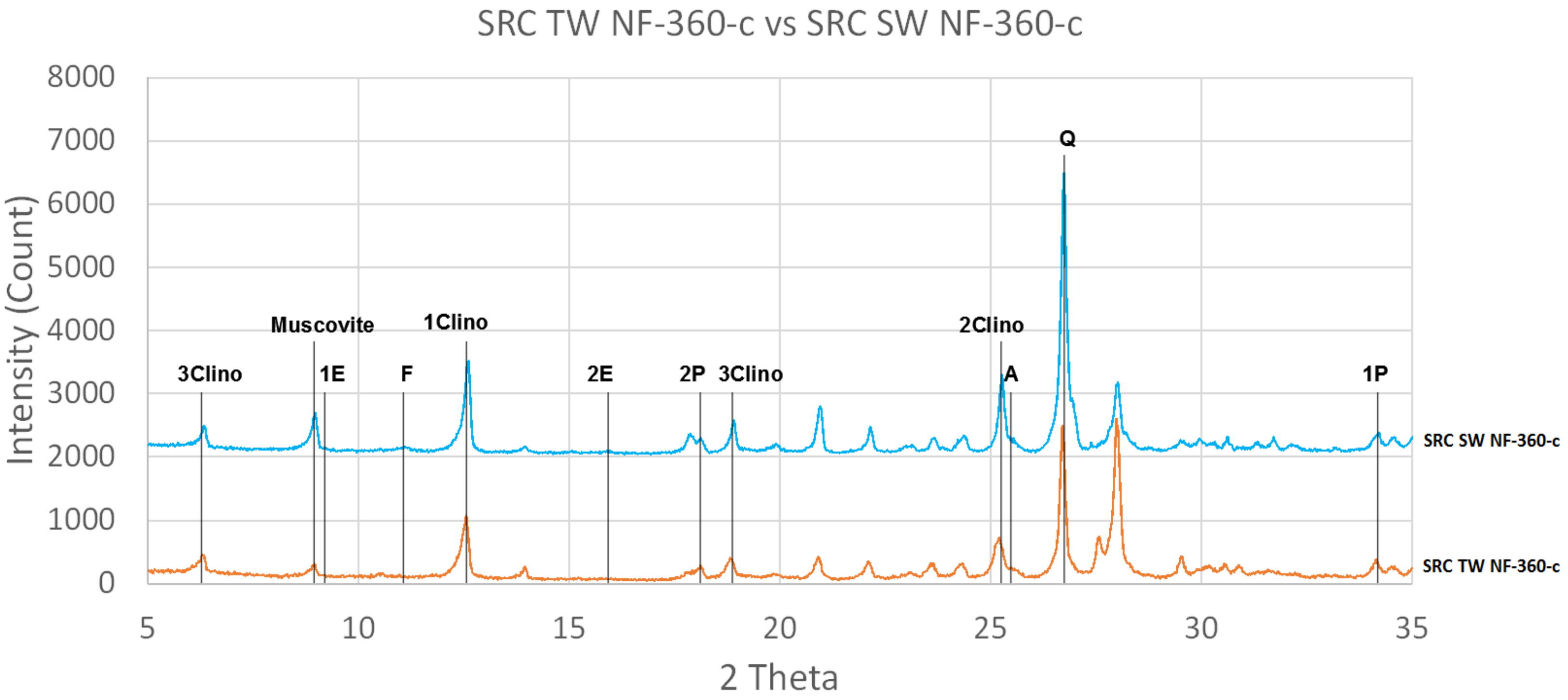


Figure A.10. SRC TW NF-270-s vs SRC SW NF-270-s



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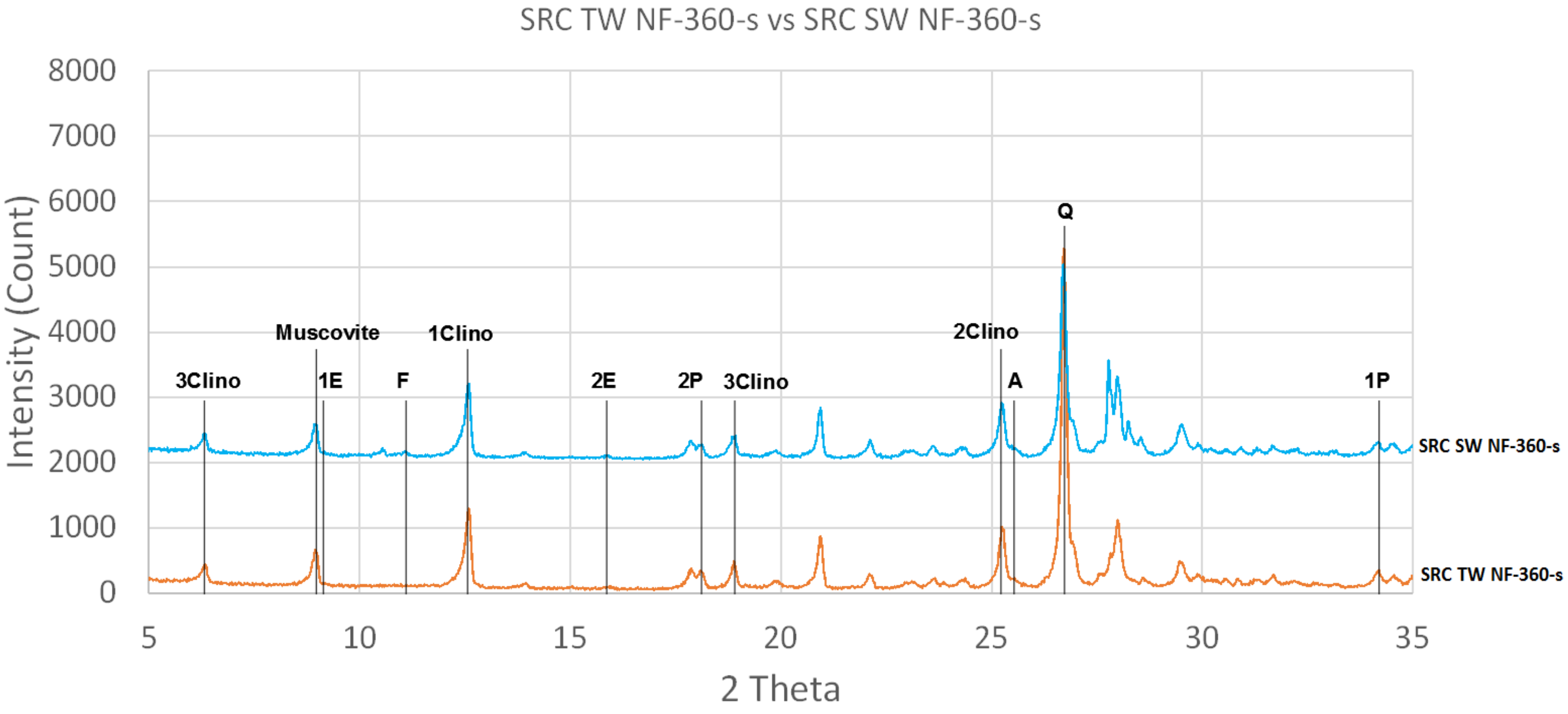


Figure A.12. SRC TW NF-360-s vs SRC SW NF-360-s

APPENDIX B: GRAPHICAL RESULTS OF BINDER COMPARISON

The graphical XRD results of the comparison of PC and SRC concrete samples from 28th day to 360th day were shown.

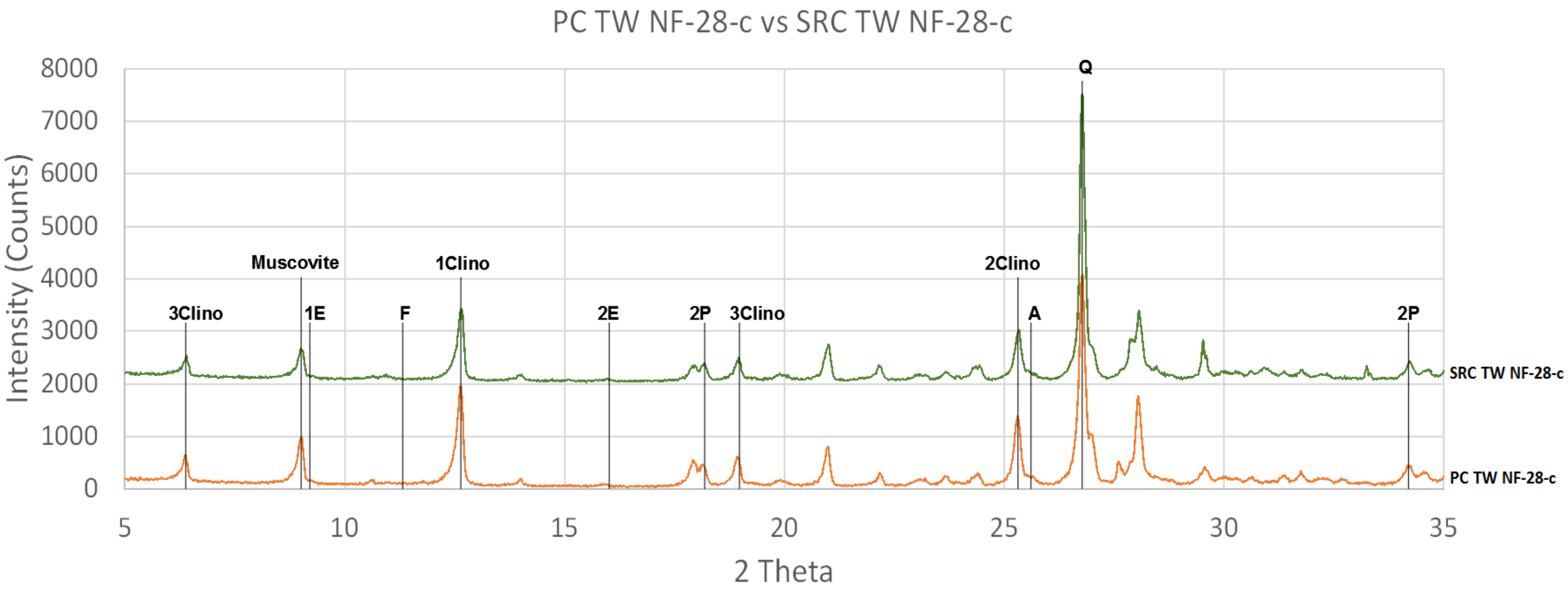


Figure B.1. PC TW NF-28-c vs SRC TW NF-28-c

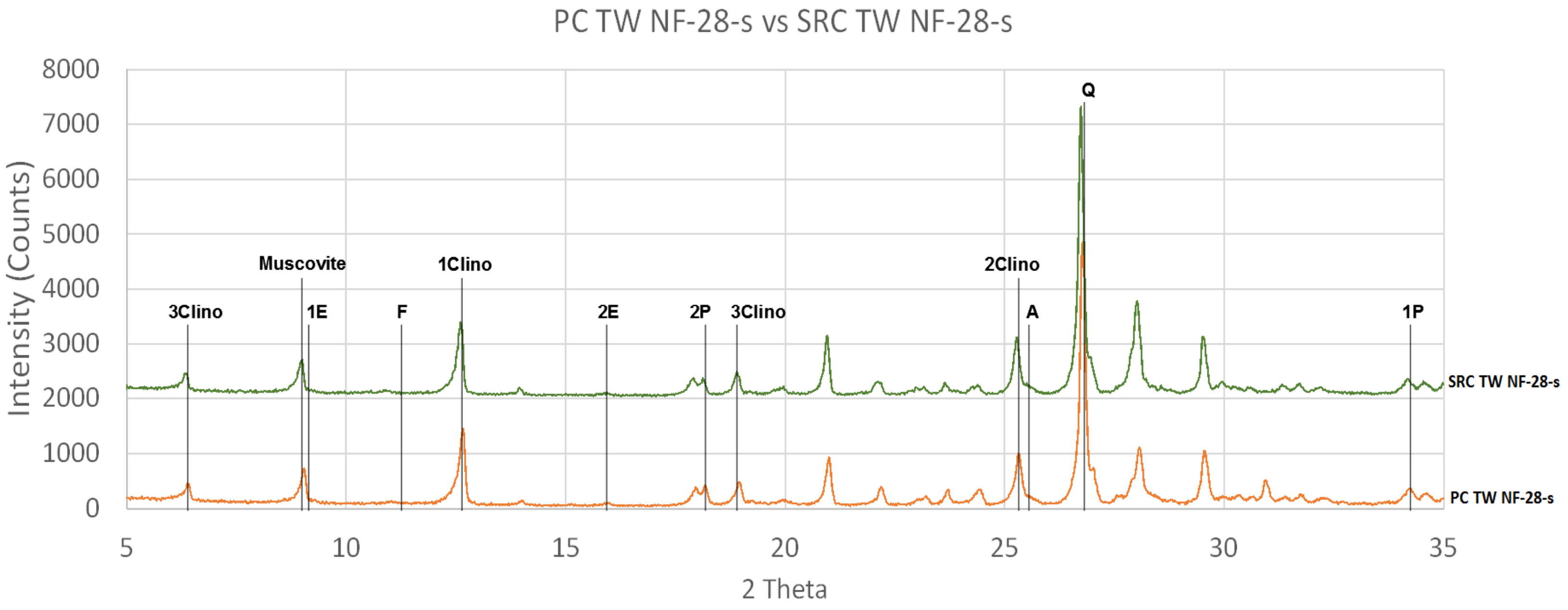


Figure B.2. PC TW NF-28-s vs SRC TW NF-28-s

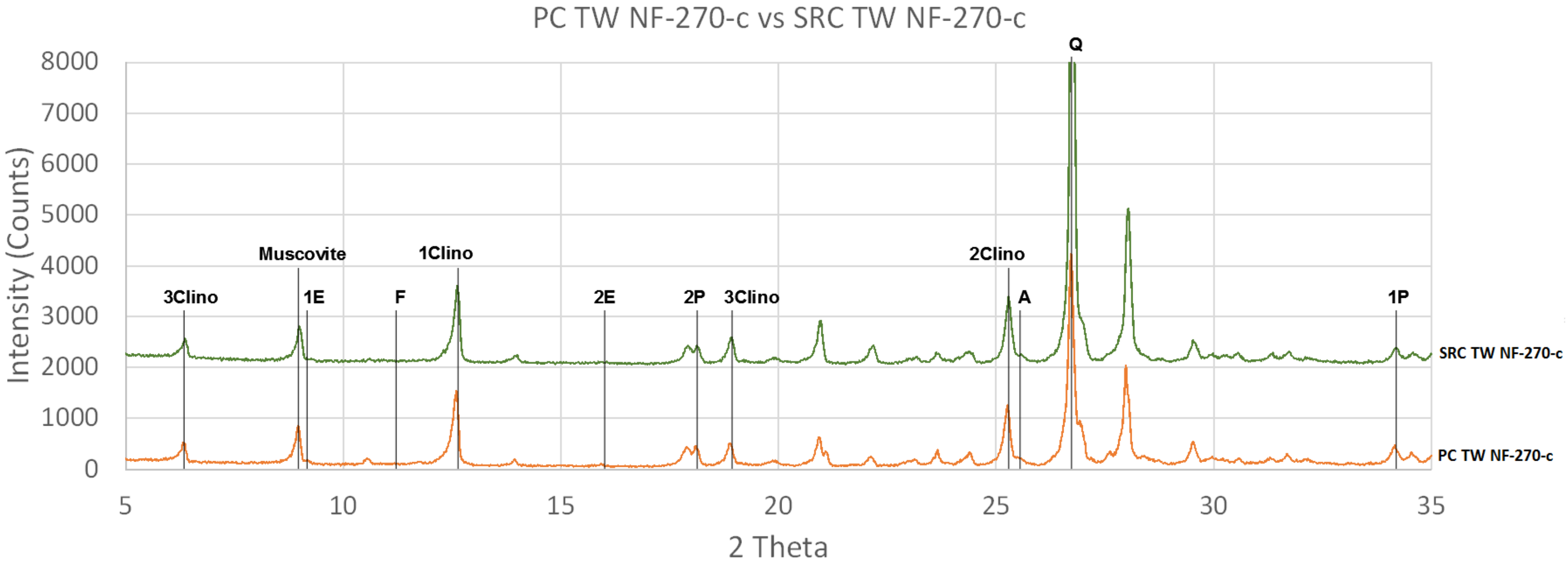


Figure B.3. PC TW NF-270-c vs SRC TW NF-270-c

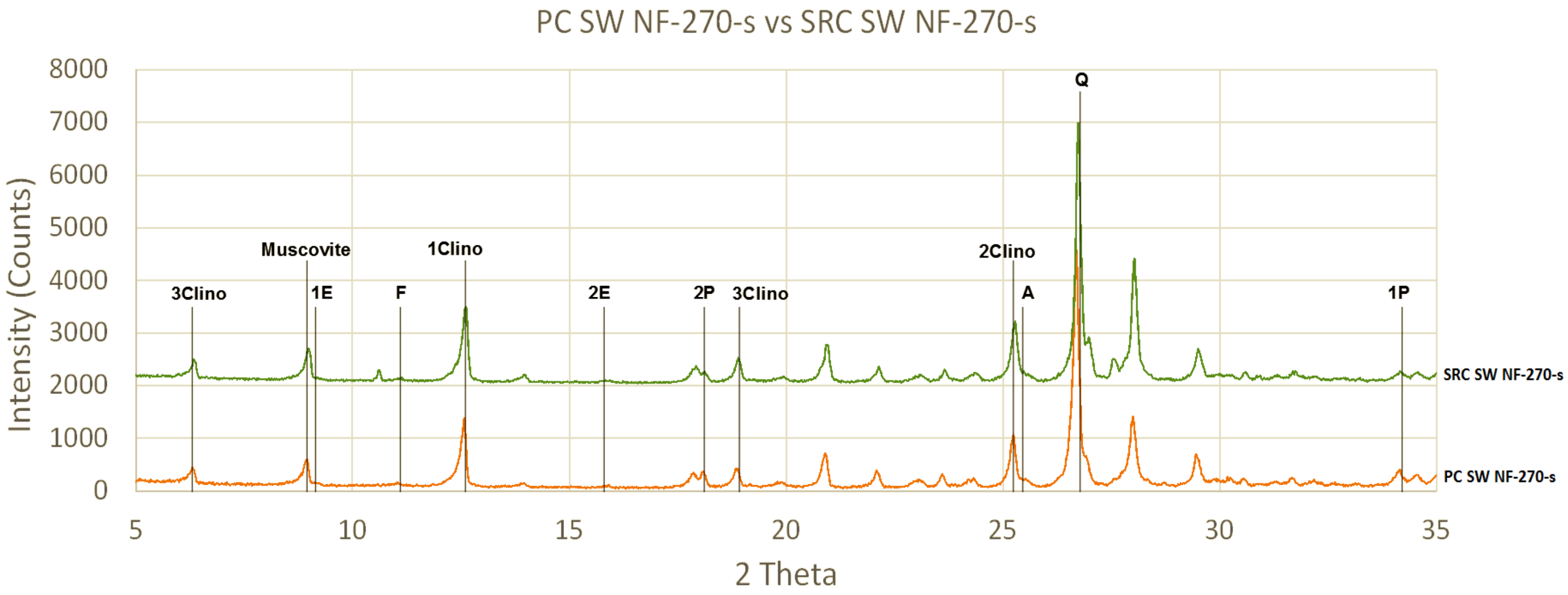


Figure B.4. PC TW NF-270-s vs SRC TW NF-270-s

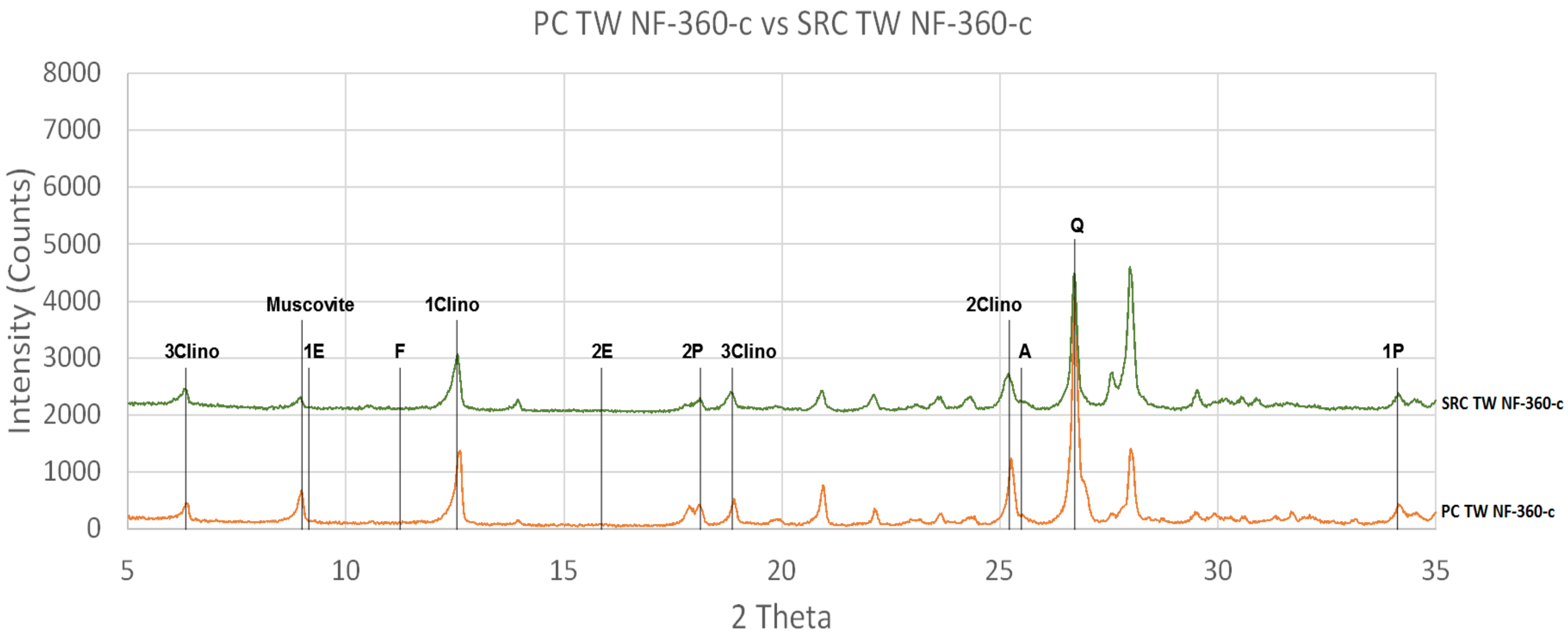


Figure B.5. PC TW NF-360-c vs SRC TW NF-360-c

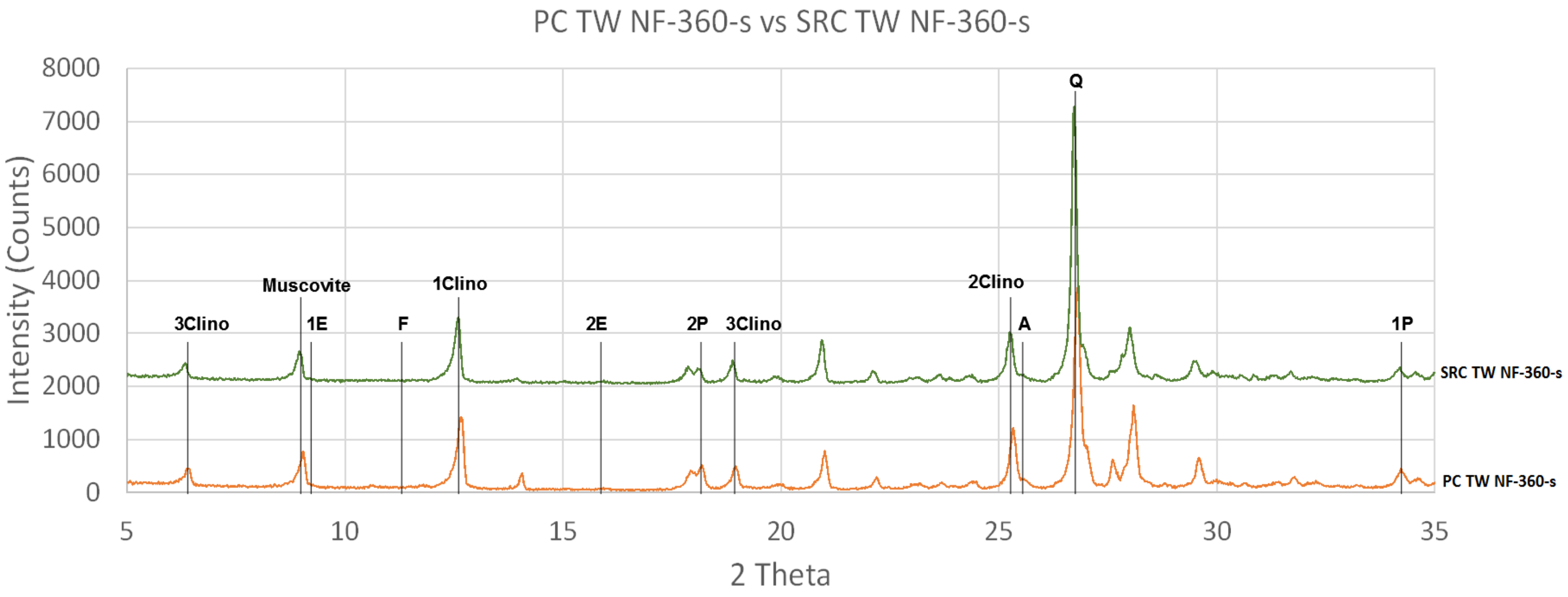


Figure B.6. PC TW NF-360-s vs SRC TW NF-360-s

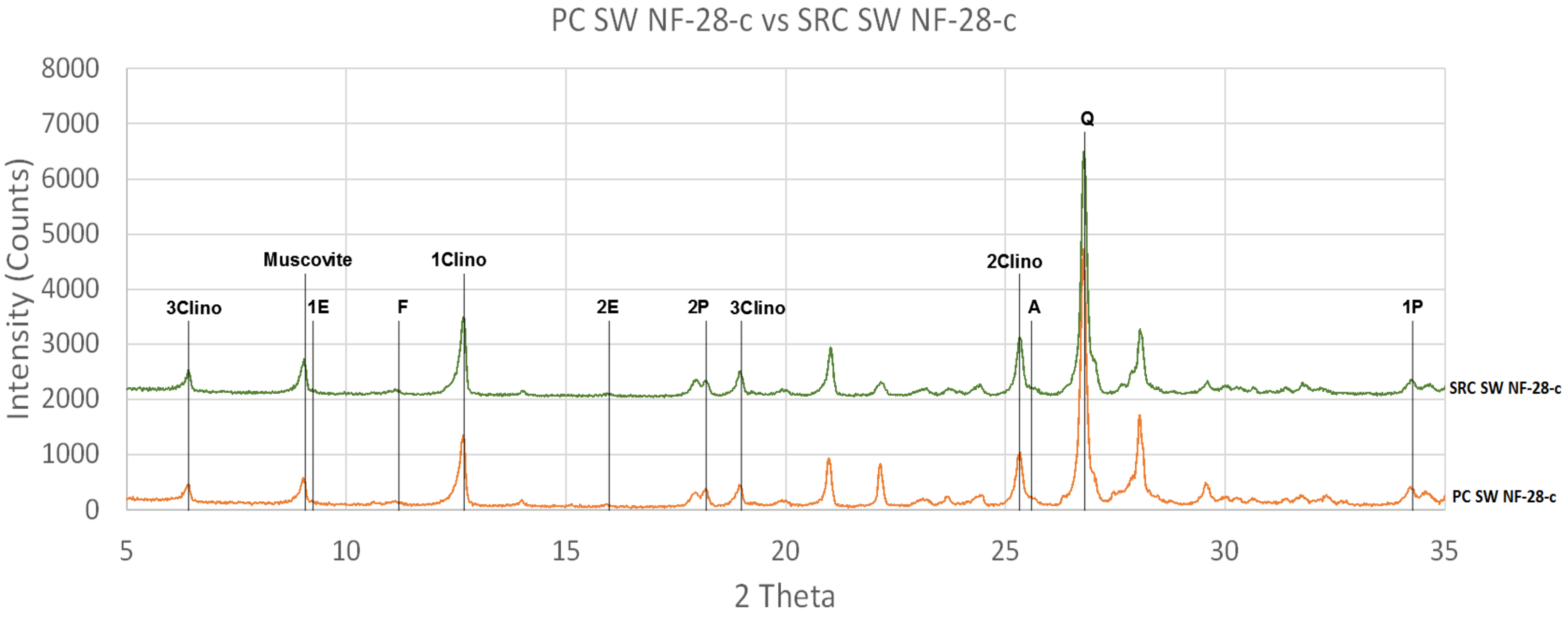


Figure B.7. PC SW NF-28-c vs SRC SW NF-28-c

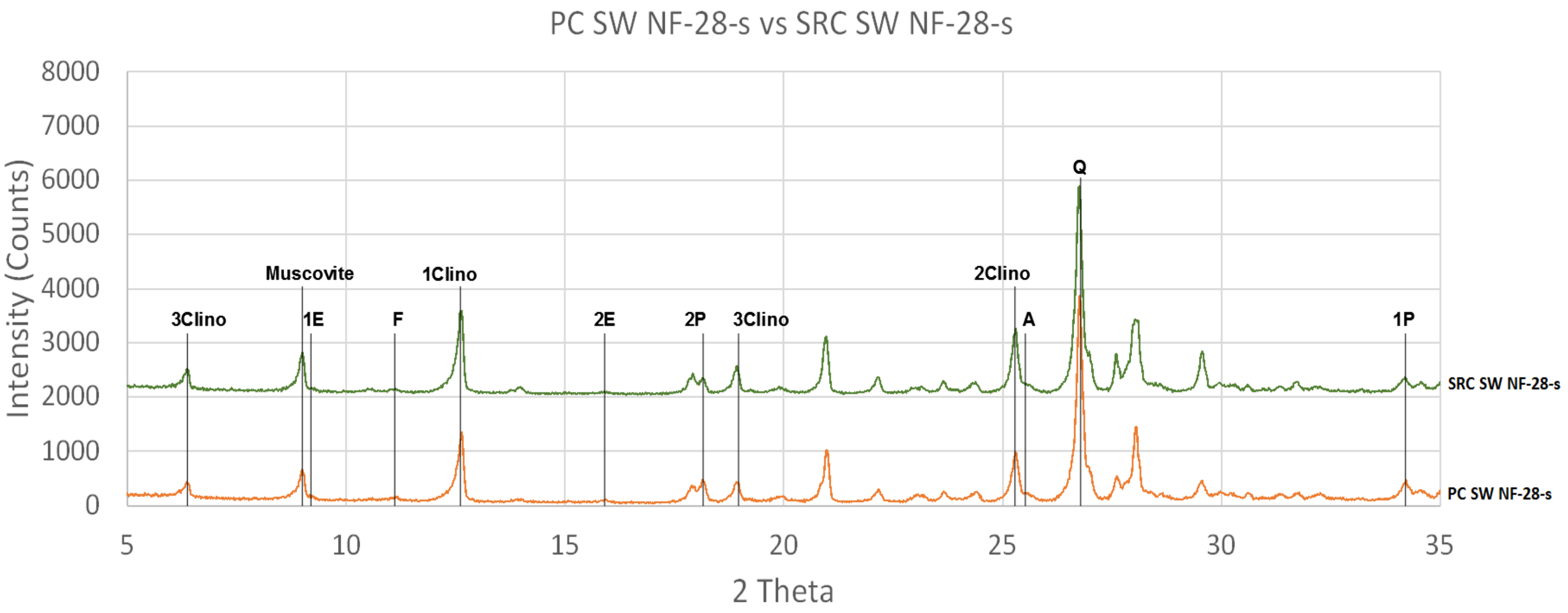
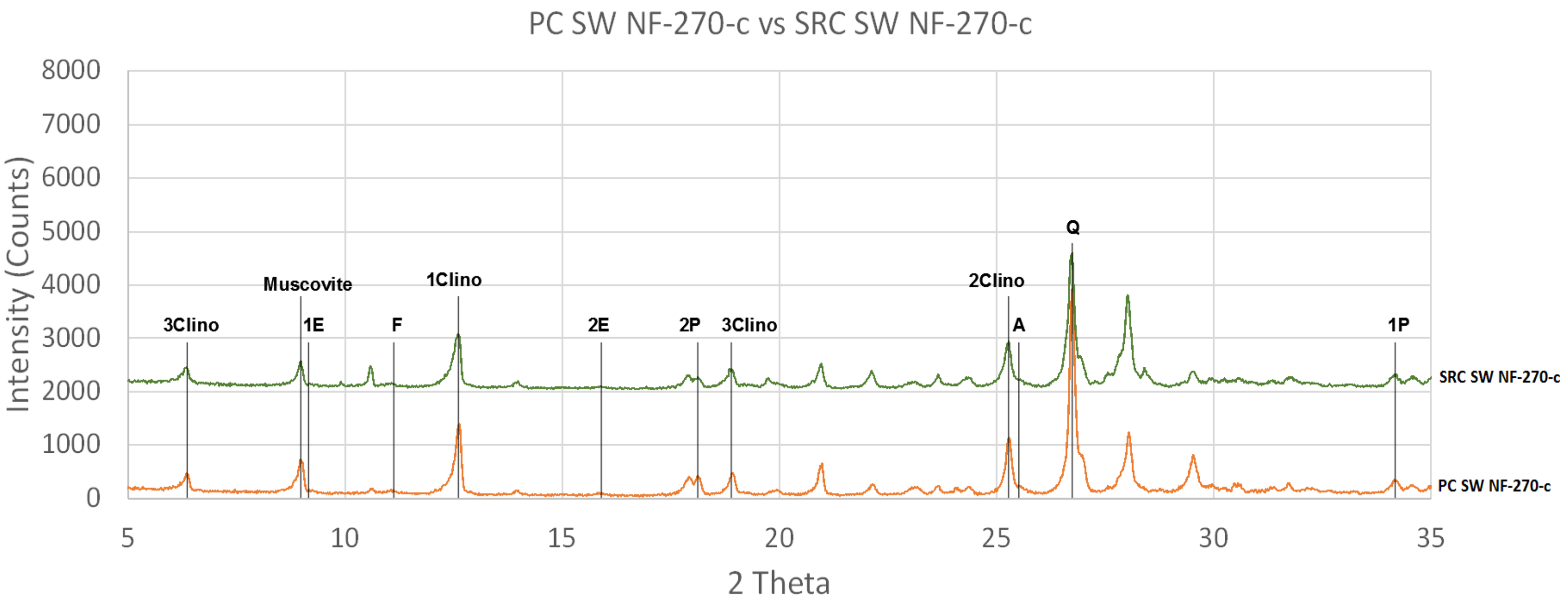


Figure B.8. PC SW NF-28-s vs SRC SW NF-28-s



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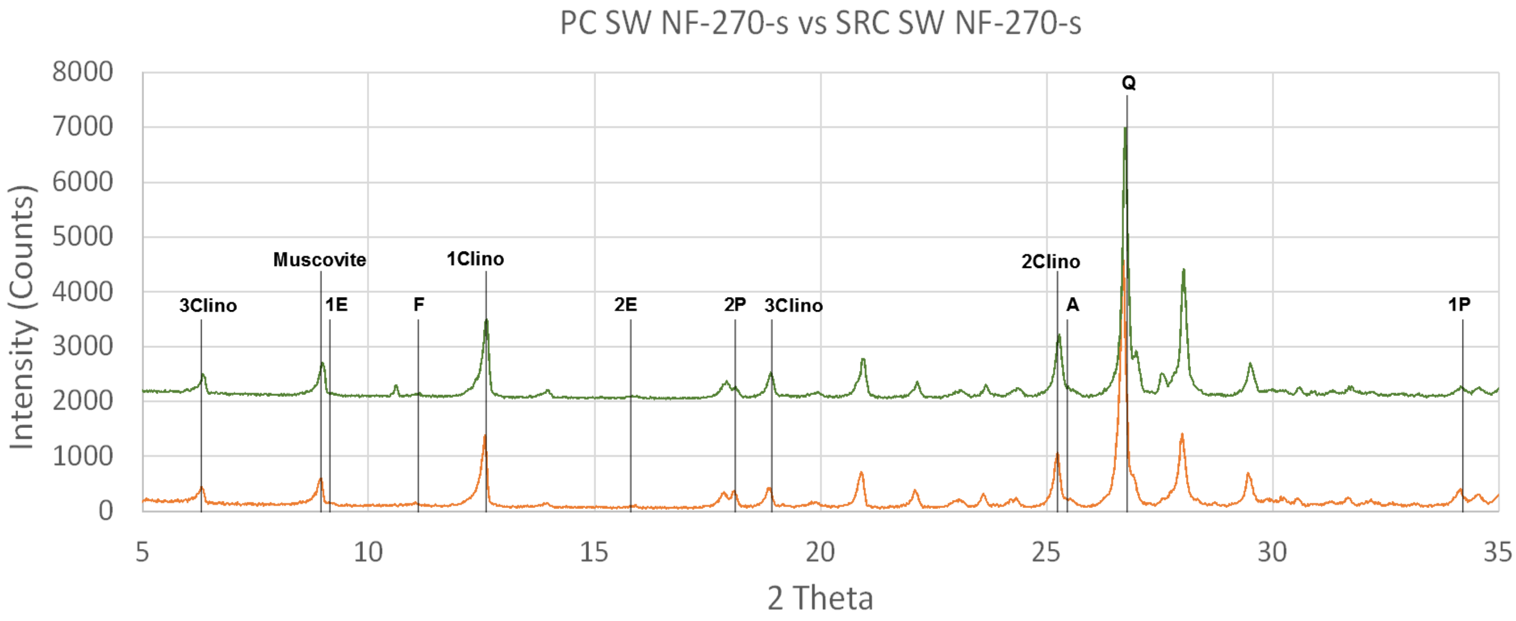

Figure B.10. PC SW NF-270-s vs SRC SW NF-270-s

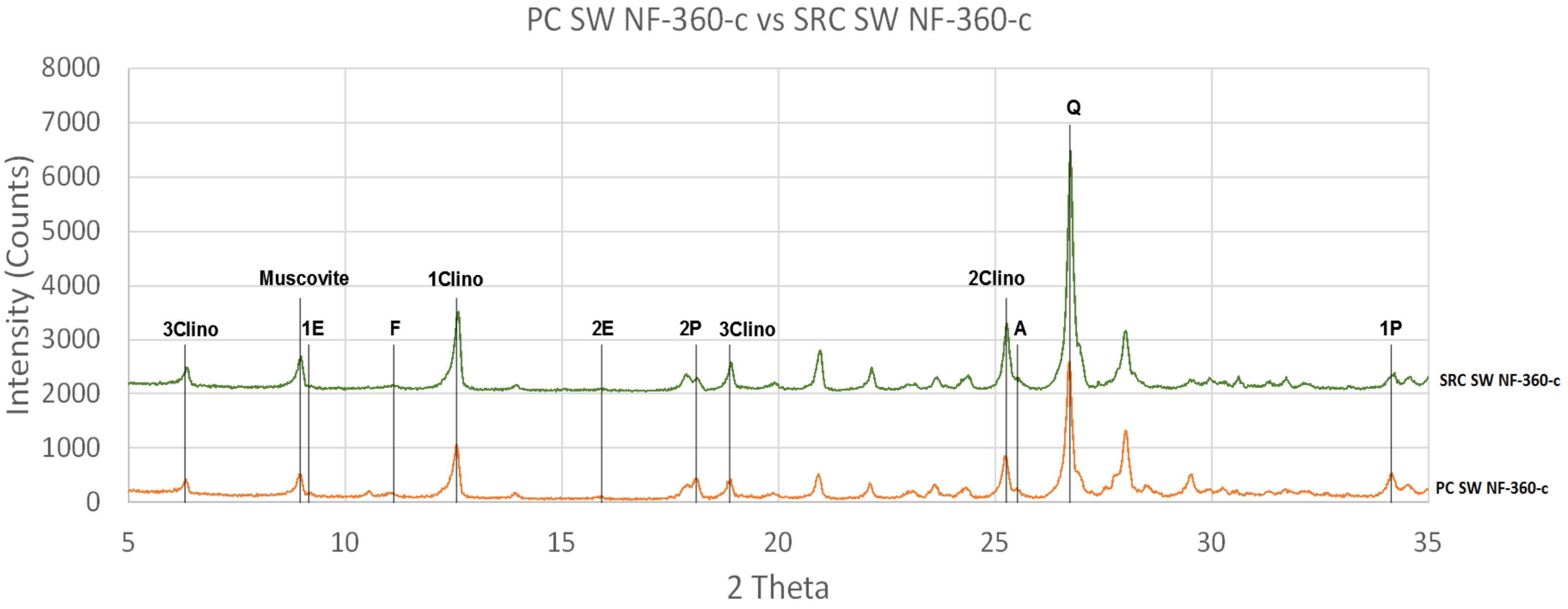

Figure B.11. PC SW NF-360-c vs SRC SW NF-360-c

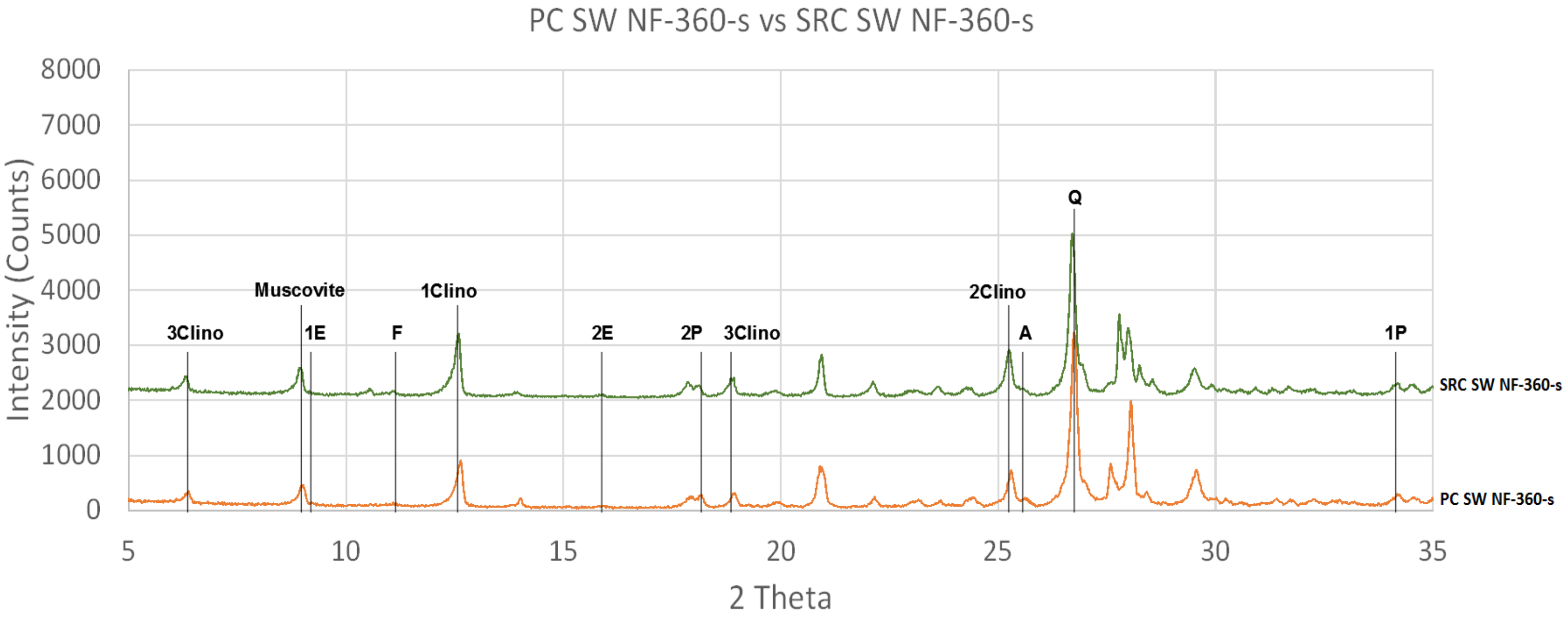

Figure B.12. PC SW NF-360-s vs SRC SW NF-360-s