# CHAPTER IV

## RESULTS AND DISCUSSION

### 4.1 Chloride diffusion coefficient:

*4.1.1 Ordinary Portland cement case:*

After conducting the test, concrete specimens were removed, split by using diamond saw and sprayed on the cut surfaces with 0.1M silver nitrate solution. By measuring the depth of the visible brown part on the split specimen surface, chloride penetration depths of those specimens were obtained and then chloride diffusion coefficient were computed and presented in Table 4.1 with ordinary Portland cement case.

**Table 4.1** Chloride diffusion coefficient for ordinary Portland cement case

| No | w/b | Average chloride depth $X_d$ (mm) | | | Diffusion coefficient ($10^{-12}$ $m^2/s$) | | |
|---|---|---|---|---|---|---|---|
| | | 1st specimen | 2nd specimen | 3rd specimen | 1st specimen | 2nd specimen | 3rd specimen |
| D.1 | 0.4 | 22.13 | 22.13 | 23.88 | 22.88 | 23.88 | 22.88 |
| D.12 | 0.5 | 30.75 | 30.75 | 30.25 | 30.71 | 30.25 | 30.71 |
| D.23 | 0.6 | 42.34 | 42.34 | 41.88 | 40.88 | 41.88 | 40.88 |

Generally speaking, the value of chloride diffusion coefficient increases with decrease of water binder ratio. The higher water binder ratio is the larger chloride diffusion coefficient is.

Obviously, it is well known that the chloride diffusion coefficient strongly depends on the porosity and pore size distribution of cement paste. The chloride movement mainly depends on the pores and their sizes inside the concrete specimen which in turn, the water binder ratio. In addition, the cement paste formed by the hydration reactions always contains interconnected pores of different sizes. The pores can be basically divided into macro pores, capillary pores and gel pores. Normally, gel pores have dimensions ranging from a few fraction of an nm to several nm (Luca Bertolini el al 2003). They do not affect the chloride ingress resistance of concrete structures because they are too small to allow significant transport of chloride ions. The capillary pores are the voids not filled by the solid products of hydration and usually have dimensions from 10 to 50 nm if the cement paste is well hydrated and produced using low water binder ratio, however can reach up to 3 – 5 μm if the concrete is made using high water binder ratio or it is not well hydrated (Luca Bertolini el al 2003). Capillary pores are relevant directly to the durability of concrete and its protection of the reinforcement. Water binder ratio and the degree of hydration are the main factors that determine the capillary porosity. Capillary pores in the cement paste increases with the amount of water used and thus with the water binder ratio and decreases with the degree of hydration, i.e. the fraction of hydrated cement (Powers 1958). Moreover, there is another conclusion from Mehta and Manmohan 1979 that decreasing water binder ratio and increasing degree of hydration of cement, both the volume and size of large pores are reduced, thereby causing a reduction of the permeability of the hardened cement paste. Furthermore, a clear effect of water binder ratio on the diffusion coefficient is also concluded by Frederiksen el al. 1996. In addition, Mehta 1980 also stated that by increasing the water binder ratio by a value of 0.10 the permeability may easily rise by a factor 10.

Figure 4.1 presents the data points for the current case and also shows the expression developed by curve fitting. This proposed expression is used for predicting service life of concrete structure which will be discussed in chapter 5 later on. Furthermore, there also present values of chloride diffusion coefficient from Yang and Wang 2003.

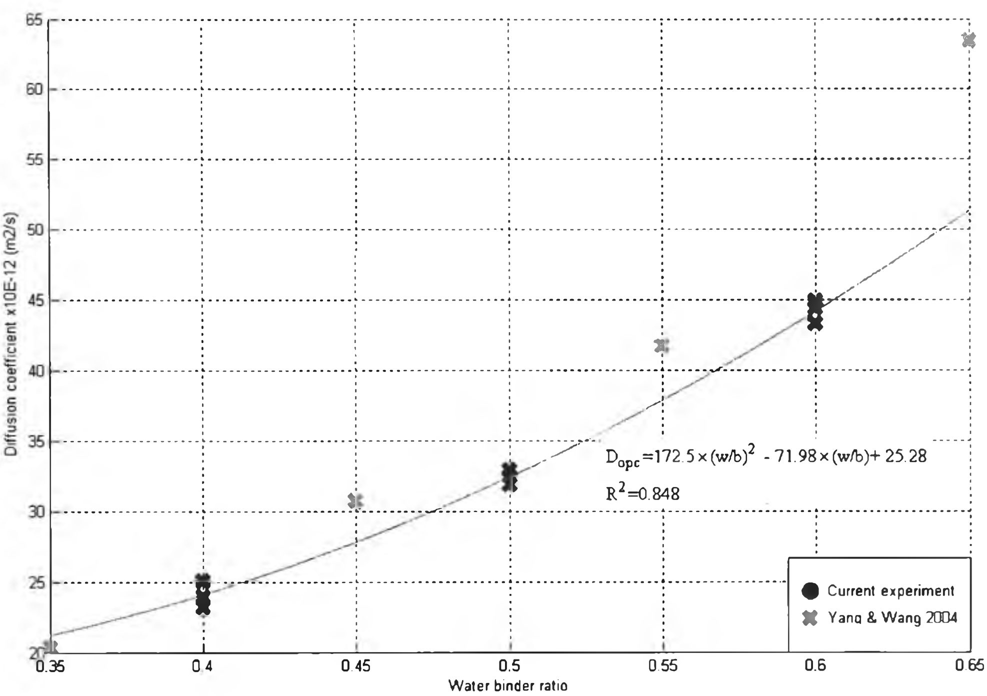


**Figure 4.1** Experiment data for ordinary Portland cement case.

From the above figure, obviously water binder ratio 0.2 is the turning point for the expression. It means that after water binder ratio 0.2, the chloride diffusion coefficient will grow up. It does not correspond to the theorical background which states that the smaller water binder ratio, the lower chloride diffusion coefficient. However, it is very difficult and not common to achieving water binder ratio that is smaller than 0.2. In addition, by indicate the applicable range with the minimum water binder ratio of 0.27, the above expression can be still applied and obey the theorical background. The water binder ratio 0.27 is chosen because it is the minimum point for the application range of high strength concrete structures.

Yang and Wang expressed the relationship of chloride diffusion coefficient in term of water binder ratio by the linear fashion. However, it is not correct in theory because it is well known that the relationship between chloride diffusion coefficient and water binder ratio, which in turn, the relationship between porosity and water binder ratio is non-linear (see figure 4.2). Therefore, in the current case, chloride diffusion coefficient is proposed in non-linear relationship in term of water binder ratio.

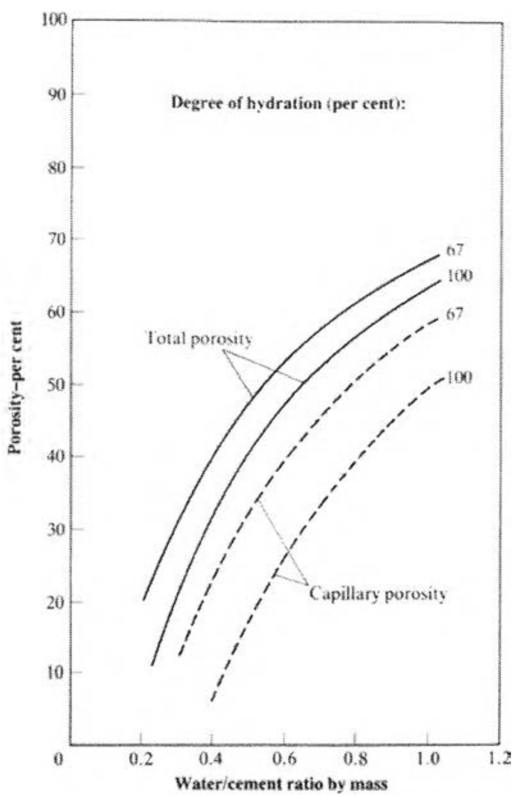


**Figure 4.2** Relationship between water binder ratio and the total porosity (Powers 1958)

According to the mix proportion presented in previous chapter, obviously the current case takes in account two different parameters that are water binder ratio and binder content when investigating the chloride diffusion coefficient. However, the proposed expression for ordinary Portland cement case is expressed in term of only water binder ratio. It can be explained by the chloride binding isotherm. Generally speaking, chloride ingress is a complex phenomenon involving various factors. And the basic parameters that should be considered when studying chloride diffusion coefficient in concrete structure are essentially the diffusion characteristics of concrete which is affected by the physical nature of the interconnected pores and the chloride binding capacity of concrete. While the former is governed directly by water binder ratio and degree of hydration, chloride binding capacity is a function of binder content and binder type. In the first case, we speak of free chloride and in the second case, of bind chloride. Both of them are used to determine the total amount of chloride ions moving into concrete structures. Free chloride is usually defined as the amount of chloride dissolved in the pore solution and bind chloride on the other hand is defined as the amount of chloride chemically react with the hydration compounds of cement, particularly with $C_3A$, to form calcium chloroaluminate (known as Friedel salts). It is generally recognized that only the free chloride ions influence the degradation of reinforced concrete. Therefore, in the current study, only free chloride is considered and in turn, the expression of chloride diffusion coefficient for case of ordinary Portland cement is proposed in term of only water binder ratio. In addition, the details of the experiment of Yang and Wang 2003 can be seen in appendix.

*4.1.2 Case of partial replacement by pozzolan:*

In order to investigate the influences of pozzolan on the ordinary Portland cement case, chloride diffusion coefficient are also studied with cases of partial replacement of ordinary Portland cement by equivalent mass of fly ash, rice husk ash and with case of triple blend, respectively.

*4.1.2.1 Case of partial replacement by fly ash:*

The results of chloride diffusion coefficient for the current case are presented in table 4.2. Moreover, some data from the experiments of Yang and Wang are presented as well in figure 4.3. The chloride diffusion coefficient from Yang and Wang experiments is significantly smaller than the current case. This can be explained due to the different in the amount of $SiO_2$ in fly ash composition. $SiO_2$ in Yang and Wang 2003 is about 56.7%, which is higher approximately three times than the current study, about 20.9% (see Appendix).

**Table 4.2** Chloride diffusion coefficient for fly ash case

| No. | w/b | FA | Average chloride depth $X_d$ (mm) | | | Diffusion coefficient ($10^{-12}$ $m^2/s$) | | |
|---|---|---|---|---|---|---|---|---|
| | | | **1$^{st}$ specimen** | **2$^{nd}$ specimen** | **3$^{rd}$ specimen** | **1$^{st}$ specimen** | **2$^{nd}$ specimen** | **3$^{rd}$ specimen** |
| D.5 | 0.4 | 15 | 17.13 | 16.50 | 17.88 | 17.7 | 17.0 | 18.7 |
| D.6 | 0.4 | 25 | 14.50 | 15.13 | 13.50 | 14.9 | 15.6 | 14.2 |
| D.7 | 0.4 | 35 | 12.75 | 14.25 | 13.13 | 13.4 | 15.0 | 13.8 |
| D.16 | 0.5 | 15 | 21.50 | 23.13 | 20.25 | 22.5 | 24.2 | 21.1 |
| D.17 | 0.5 | 25 | 18.50 | 19.25 | 19.13 | 19.5 | 20.3 | 20.1 |
| D.18 | 0.5 | 35 | 18.75 | 18.13 | 18.38 | 19.7 | 19.0 | 19.3 |
| D.27 | 0.6 | 15 | 29.50 | 29.13 | 30.25 | 30.8 | 30.5 | 31.6 |
| D.28 | 0.6 | 25 | 28.50 | 27.13 | 27.38 | 29.9 | 28.5 | 28.8 |
| D.29 | 0.6 | 35 | 26.38 | 25.25 | 24.50 | 27.7 | 26.5 | 25.7 |

By the same procedure as previous ordinary Portland cement case, the data points for the current case are plot and expression of chloride diffusion coefficient is proposed based on these data points. The fashion of the current proposed expression is as follows:

$$D_{FA} = D_{OPC} \times k_{FA} \tag{4.1}$$

Where:

$D_{FA}$ = chloride diffusion coefficient of fly ash case.

$D_{OPC}$ = chloride diffusion coefficient of ordinary Portland cement case, taken in account water binder ratio.

$k_{FA}$ = factor that takes in account the influence of fly ash and the sand content in addition.

The above expression is only used for case of partial replacement of Portland cement by equivalent mass of fly ash. Furthermore, unintentionally, the factor $k_{FA}$ also takes in account the influence of sand content due to vary of sand content in mix proportion. However, because as it is said earlier, the objective of the current study is only about the impact of fly ash, the effect of sand content in factor $k_{FA}$ will not be considered and investigated. In order to understand the reason why the above fashion is chosen and about the factor k as well, it should take a quick look at the fundamental mechanism that fly ash or pozzolan affects the chloride resistance of concrete structures. First of all, Portland cement is predominately composed of two calcium silicates (dicalcium silicate $C_2S$ and tricalicium silicate $C_3S$) which account for 70 percent to 80 percent of the cement and by reacting with water in hydration process, calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) are produced. C-S-H accounts for more than half the volume of hydrated cement paste while CH accounts for about 25 percent of the paste volume. The remainder of hydrated Portland cement is predominantly composed of calcium sulfoaluminates and capillary pores. Generally speaking, C-S-H is a superior reaction produce because it creates a denser microstructure that increases strength, reduces the permeability and improves the resistance to chloride ingress. On the other hand, the formation of CH increases the porosity and thus makes concrete be susceptible to chloride ingress. The pozzolanic reaction converts the soluble CH to C-S-H increasing the overall resistance to chloride ingress or decreases the chloride diffusion coefficient. Figure 4.3, 4.4 and 4.5 present the decrease of chloride diffusion coefficient when replacing partially of Portland cement by fly ash.

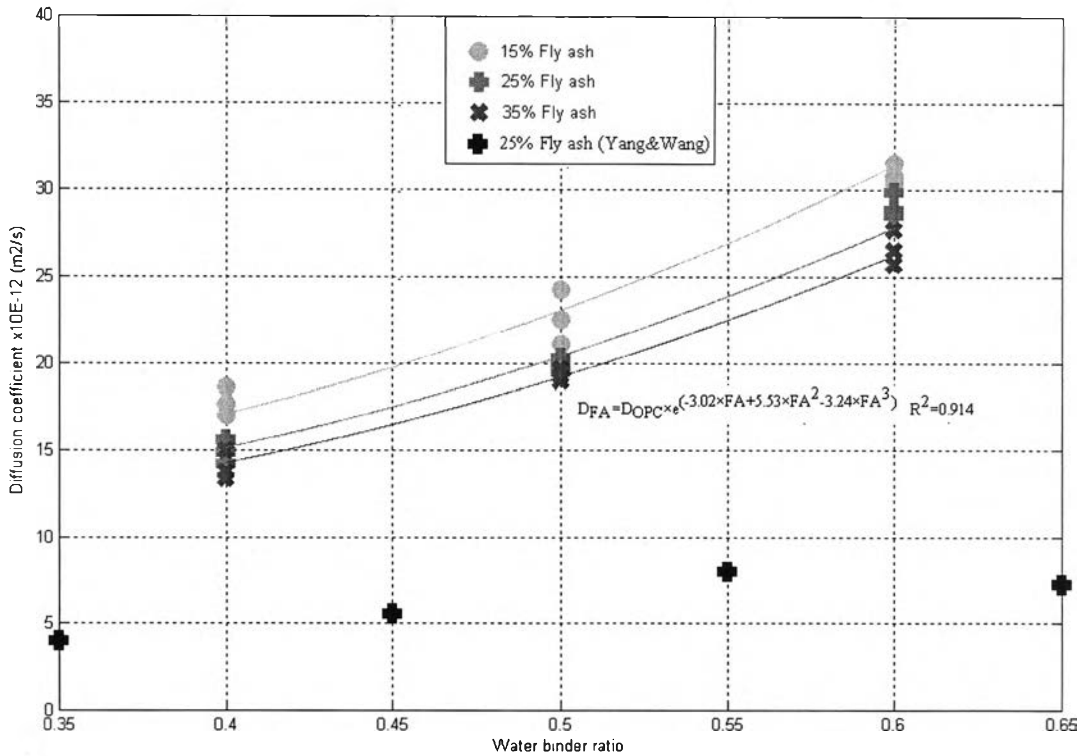


**Figure 4.3** Chloride diffusion coefficients in term of water binder ratio for fly ash case

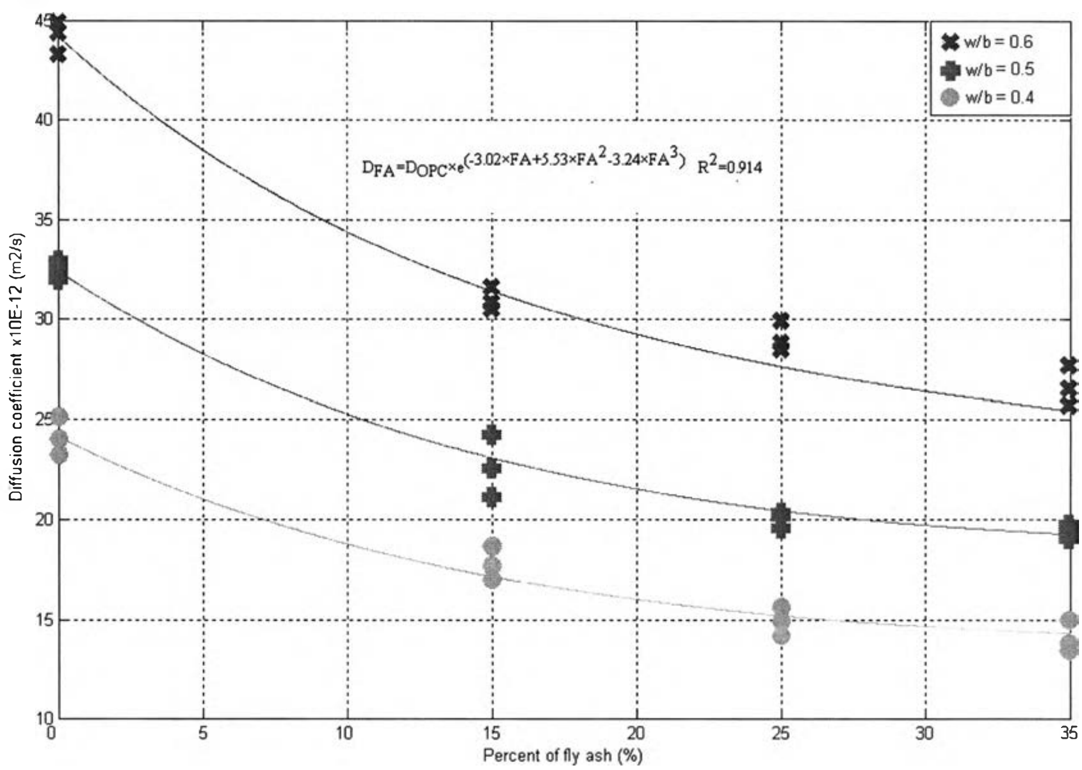


**Figure 4.4** Chloride diffusion coefficients in term of percent of fly ash for fly ash case

According to the above plots, the values of chloride diffusion coefficient in the experiments of Yang and Wang 2003 are significantly lower than these of current work. It can be explained by the amount of silicate oxide in the composition of fly ash. In case of Yang and Wang 2003, silicate oxide accounts for 56.7%, about nearly two times comparing with 33.03% for the current case (see Appendix). Therefore, the amount of C-S-H increases remarkable and then leads to the decrease significantly in chloride diffusion coefficient. In addition, the factor k for the current case is as follows:

$$k_{FA} = e^{(-3.02\times FA + 5.53\times FA^2 - 3.24\times FA^3)} \qquad (4.2)$$

Where:

$k_{FA}$ = factor that takes in account the fly ash effect.

FA = percent of fly ash

Generally, the higher amount of replacement of fly ash is, the smaller chloride diffusion coefficient is. It can be concluded that fly ash has huge impact on decrease of chloride diffusion coefficient, for example from the above graph, increase from 15% to 25% of replacement of fly ash can reduce chloride diffusion coefficient about 25%.

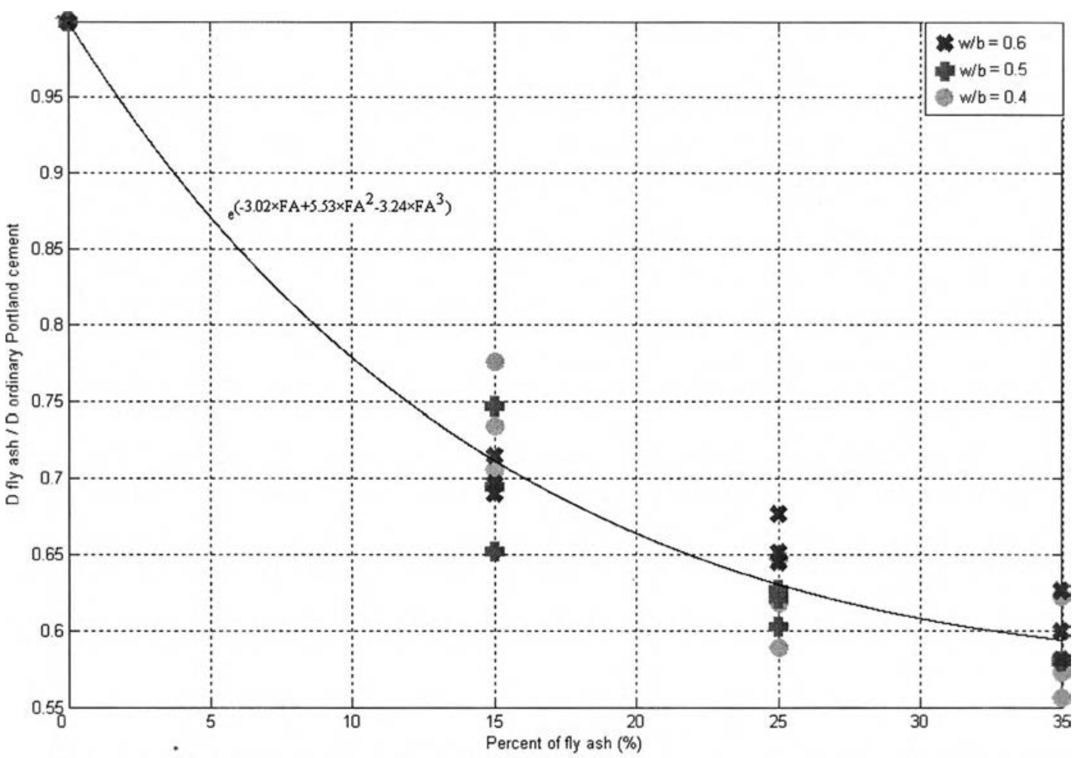


**Figure 4.5** The influence of fly ash on chloride diffusion coefficient by factor $k_{FA}$

From the above figure, obviously, the order of the values of water binder ratio is not in agreement. It means that we can not investigate the influence of fly ash on the chloride diffusion coefficient by factor $k_{FA}$ with only one equation for all three water binder ratio series because incidentally, the water binder ratio which is already investigated in the previous ordinary Portland cement case is now taken in account in the current case again. In addition, it can be explained by considering the effect of sand content unintentionally besides the influence of fly ash in factor $k_{FA}$. Therefore, in order to consider only the role of factor $k_{FA}$, three particular expressions of chloride diffusion coefficient which are correlative with three different series of water binder ratio are proposed for the current case. Furthermore, by employing different equation for each water binder ratio, we can skip the effect of water binder ratio which was investigated in the ordinary Portland cement case earlier and investigate only the impact of factor $k_{FA}$ which in turn is the influence of percent of fly ash on the chloride diffusion coefficient of ordinary Portland cement case. In addition, in order to give the comments about the application for the general expression of the current case, the comparison between the general equation for all three water binder ratio series and particular equations for three series of water binder ratio are shown in figure 4.6.

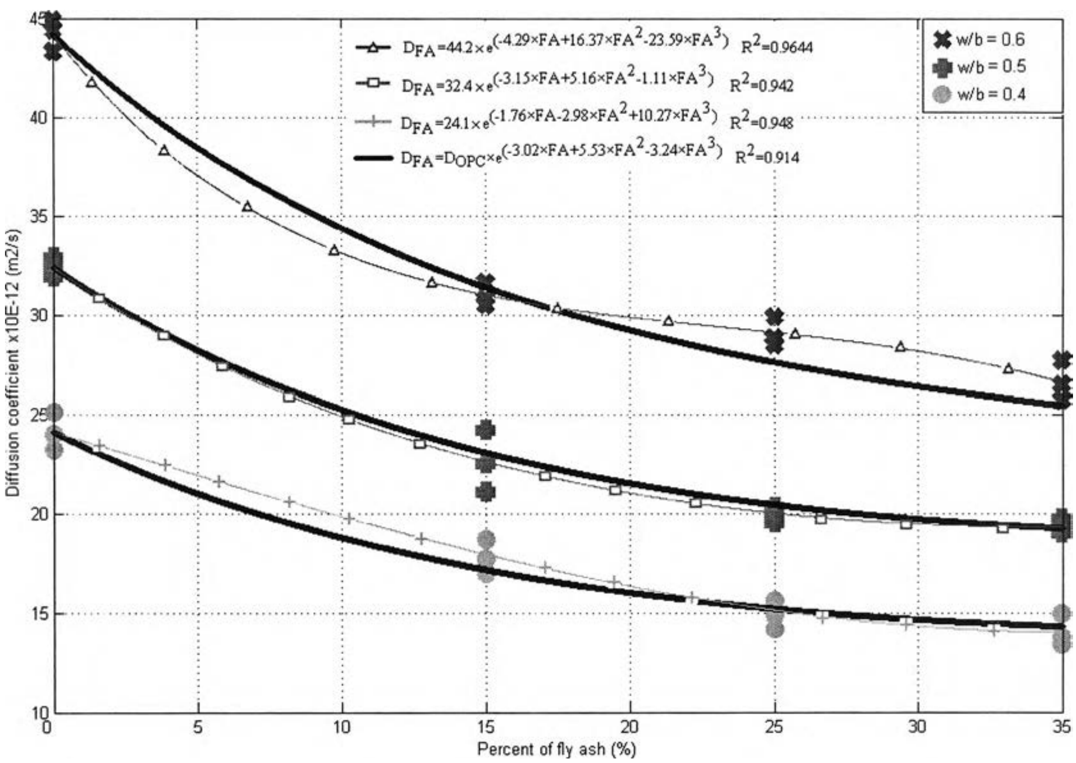


**Figure 4.6** General equation and particular equations of diffusion coefficient for different series of water binder ratio

It can be seen obviously from the figure 4.6 that with very high water binder ratio 0.6 and with larger amount of fly ash, up to 25% and 35%, the chloride diffusion coefficient is quite different between two sets of equations and for the others, there are good agreement between these two sets of equations. It can be explained by the low pozzolanic activity of fly ash because the effect of pozzolanic admixtures was found to depend on the reactivity of the pozzolan used. Normally, fly ash does not reduce the volume of capillary pores and the resistance of cement paste to chloride ingress until after 90 days (P. Kumar Mehta 1980). In addition, it can be seen from the figure that the chloride diffusion coefficients for particular case of 0.6 with 25% and 35% of fly ash are higher than the general case with same conditions. It can be explained that when replacing partially by very high amount of fly ash, for example in the current case up to 25% and 35% and with high water binder ratio of 0.6, the pozzolanic reactivity of fly ash is slower than usual. Therefore, it can be concluded that when considering the high water binder ratio 0.6 and large amount of fly ash 25% or 35%, we still can rely upon the general equation for all three water binder ratio series for the application. However, we should pay more attention when using the general equation instead of particular expression for this case. And for the other water binder ratio of 0.4 and 0.5 and even 0.6 with small amount of fly ash of 15%, the general equation can be employed without inhibition.

*4.1.2.2 Case of partial replacement by rice husk ash:*

In order to investigate the influence of rice husk ash on the chloride resistance of cement paste, the current work also considers the case of partial replacement of Portland cement by equivalent mass of rice husk ash with the range of 5%, 10% and 15%. Table 4.3 shows the data of chloride diffusion coefficient obtained from the experiments.

**Table 4.3** Chloride diffusion coefficient for case of rice husk ash

| No. | w/b | RHA | Average chloride depth $X_d$ (mm) | | | Diffusion coefficient ($10^{-12}$ $m^2/s$) | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1st specimen | 2nd specimen | 3rd specimen | 1st specimen | 2nd specimen | 3rd specimen |
| D.2 | 0.4 | 5 | 11.13 | 11.50 | 10.25 | 11.5 | 11.9 | 10.5 |
| D.3 | 0.4 | 10 | 8.25 | 7.13 | 7.88 | 8.4 | 7.2 | 8.0 |
| D.4 | 0.4 | 15 | 6.25 | 7.38 | 6.88 | 6.3 | 7.5 | 7.0 |
| D.13 | 0.5 | 5 | 13.38 | 14.88 | 13.75 | 13.9 | 15.5 | 14.2 |
| D.14 | 0.5 | 10 | 10.13 | 9.38 | 9.75 | 10.4 | 9.6 | 10.0 |
| D.15 | 0.5 | 15 | 11.00 | 10.13 | 9.50 | 11.3 | 10.4 | 9.8 |
| D.24 | 0.6 | 5 | 20.25 | 19.13 | 20.50 | 21.2 | 20.0 | 21.5 |
| D.25 | 0.6 | 10 | 15.25 | 13.13 | 14.88 | 15.7 | 13.6 | 15.5 |
| D.26 | 0.6 | 15 | 15.50 | 12.13 | 13.25 | 16.1 | 12.5 | 13.7 |

Generally speaking, both rice husk ash and fly ash are classified in the same pozzolan category even though they have different origins. Both rice husk ash and fly ash have pozzolanic reactivity, not hydraulic reactivity. Therefore, they have the same mechanism in increasing the resistance of ordinary Portland cement to chloride diffusion process. It means that rice husk ash also increase the amount of C-S-H gel in cement paste by the reaction of $SiO_2$ with $Ca(OH)_2$. The C-S-H gel after that help to create a denser microstructure that increases strength, reduces the permeability and improves the resistance to chloride diffusion process. Therefore, by applying the same concept as for previous fly ash case, the expression of chloride diffusion coefficient for the rice husk ash case is proposed as follows:

$$D_{RHA} = D_{OPC} \times k_{RHA} \tag{4.3}$$

Where:

$D_{RHA}$ = chloride diffusion coefficient of rice husk ash case.

$D_{OPC}$ = chloride diffusion coefficient of ordinary Portland cement case, taken in account water binder ratio.

$k_{RHA}$ = factor that takes in account the influence of rice husk ash and sand content.

The above expression is only used for case of partial replacement of Portland cement by equivalent mass of rice husk ash. Furthermore, unintentionally, the factor $k_{FA}$ also takes in account the influence of sand content due to vary of sand content in mix proportion. However, because as it is said earlier, the objective of the current study is only about the impact of fly ash, the effect of sand content in factor $k_{FA}$ will not be considered and investigated. Figure 4.7 and 4.8 present the chloride diffusion coefficient of the current case in term of water binder ratio and percent of partial replacement of Portland cement by rice husk ash, respectively.

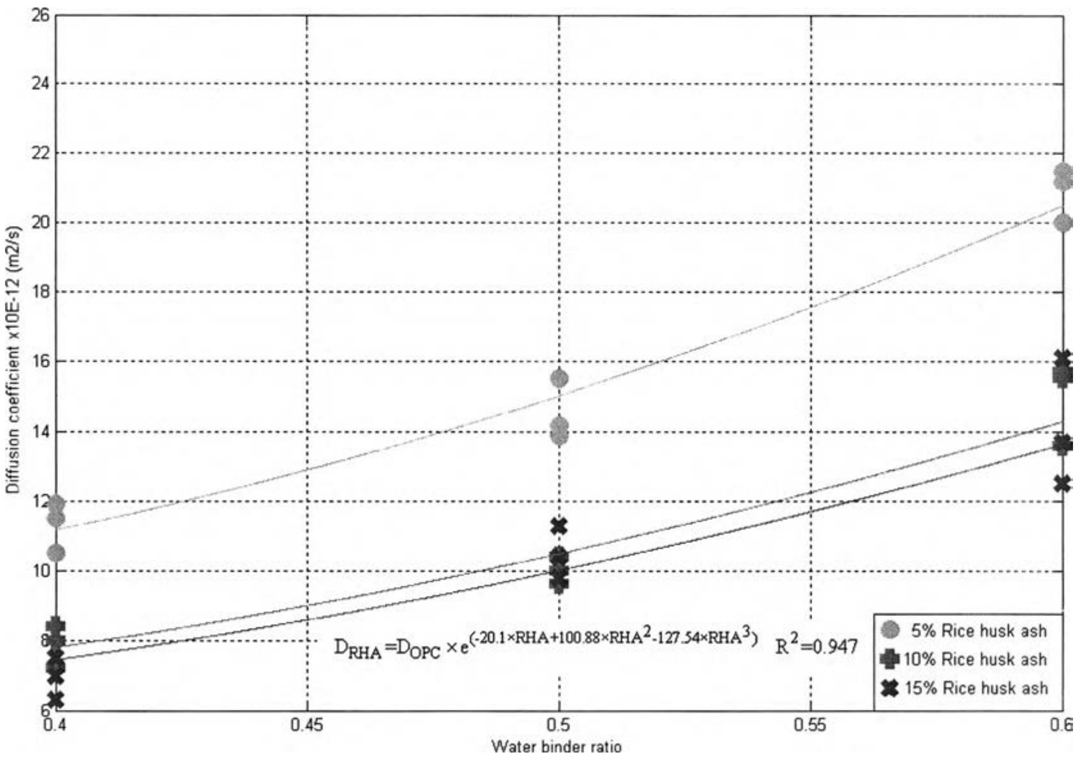


**Figure 4.7** Chloride diffusion coefficients in term of water binder ratio for rice husk ash case

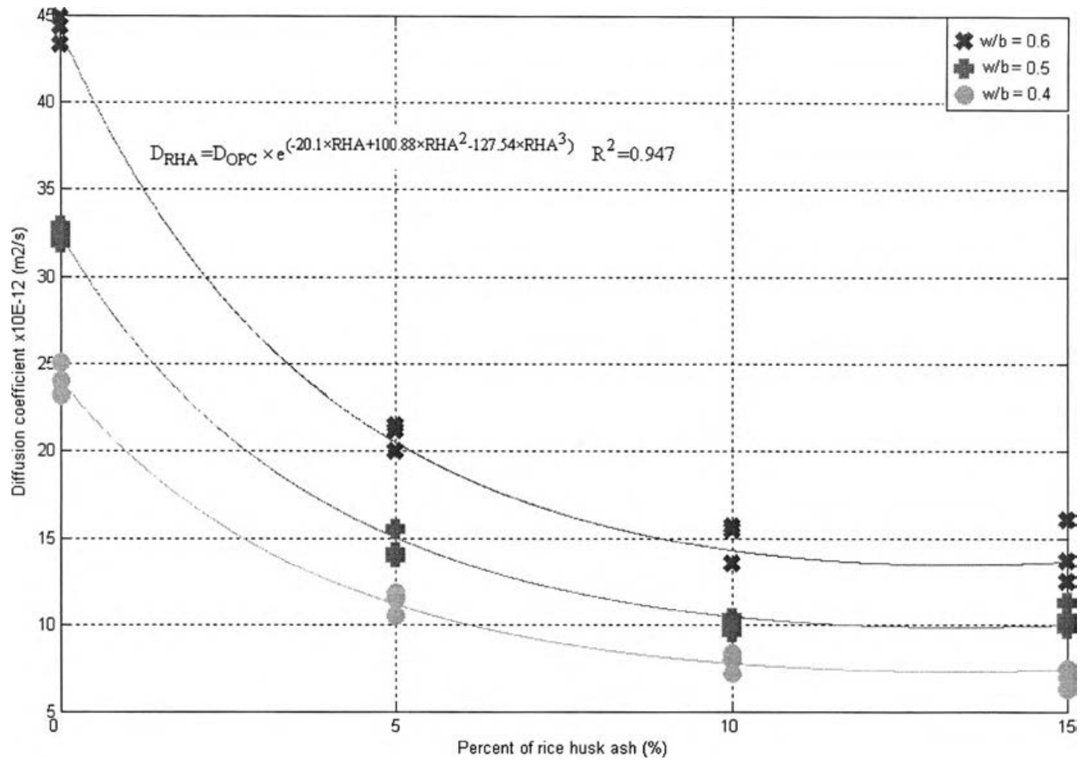


**Figure 4.8** Chloride diffusion coefficients in term of percent of rice husk ash for rice husk ash case

From the above graphs, obviously, rice husk ash shows remarkable impact on the chloride resistance. The higher percent replacement of rice husk ash, the chloride diffusion coefficient becomes obviously smaller. Even with a small amount of replacement of rice husk ash, for example 5% in the current case, the influence is also quite clear. However, when replacing up to 15 percent of rice husk ash, chloride diffusion coefficient does not decrease significantly, comparing with 10 percent case. It can be concluded that 10 percent of replacement of Portland cement by rice husk ash is the optimal point. Furthermore, when compare with fly ash case, it can be seen that the influence of rice husk ash on chloride diffusion coefficient is more noticeable. It can be explained by the manner of reactivity of these pozzolan. According to the composition of rice husk ash, the amount of silicate oxide is very high, about 87.74%, comparing with fly ash, about 33.03% as shown in table 3.3. Moreover, rice husk ash has extremely high surface area. These characteristics make rice husk ash be highly pozzolanic. Therefore, rice husk ash has the remarkable influence on chloride diffusion coefficient even at the early age. Figure 4.9 illustrates how much rice husk ash reduces the chloride diffusion coefficient as compared with ordinary Portland cement case. In addition, the factor $k_{RHA}$ for this case is as follows:

$$K_{RHA} = e^{(-20.1\times RHA + 100.88\times RHA^2 - 127.54\times RHA^3)} \tag{4.4}$$

Where:

$k_{RHA}$ = factor that takes in account the rice husk ash effect.

RHA = percent of rice husk ash

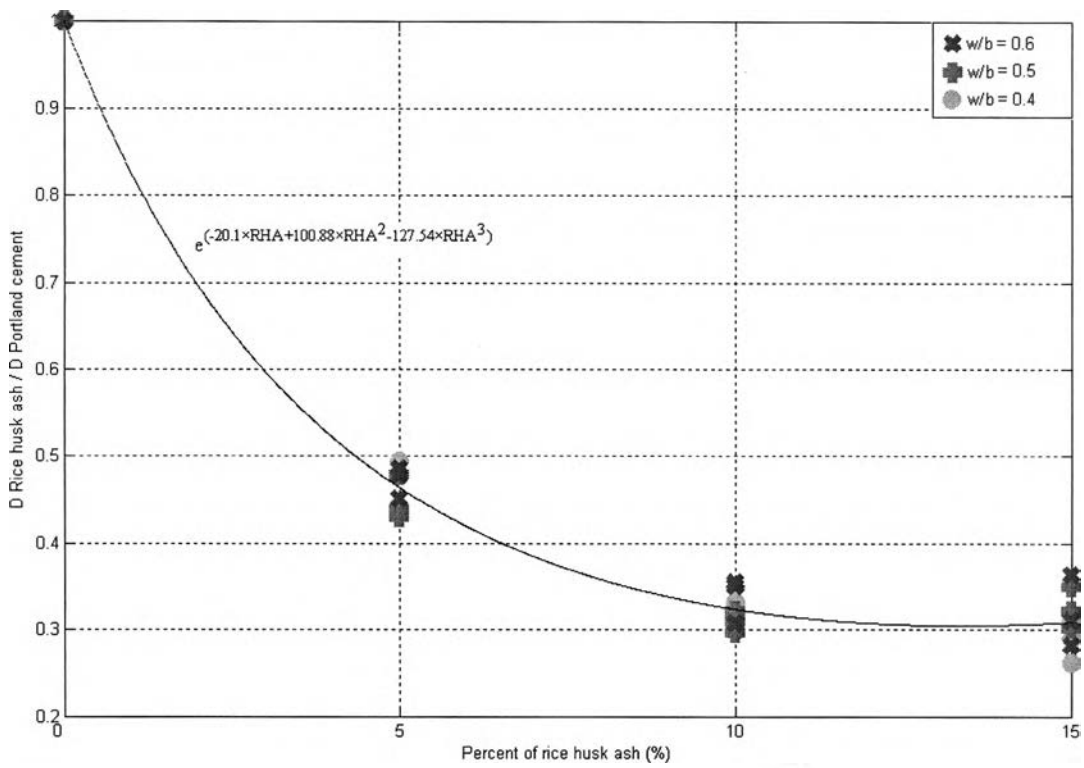


**Figure 4.9** The influence of rice husk ash on chloride diffusion coefficient by factor $k_{RHA}$

In compared with the previous case, the order of the values of water binder ratio for the rice husk ash case is in better arrangement around the curve of factor $k_{RHA}$. It can be explained by the high influence on ordinary Portland cement in decrease the chloride diffusion coefficient of rice husk ash due to the high pozzolanic reactivity even at the early age 28 days of rice husk ash. However, in order to investigate clearer with skipping the effect of water binder ratio which is already discussed in previous fly ash case and focusing only on the factor $k_{RHA}$ which in turn indicates the impact of rice husk ash on chloride diffusion process, the same procedure as previous fly ash case is employed. Three particular equations for each series of water binder ratio are also proposed and naturally, the comparison between general and particular equation are considered in order to investigate the application of the expressions of rice husk ash case, as shown in figure 4.10.

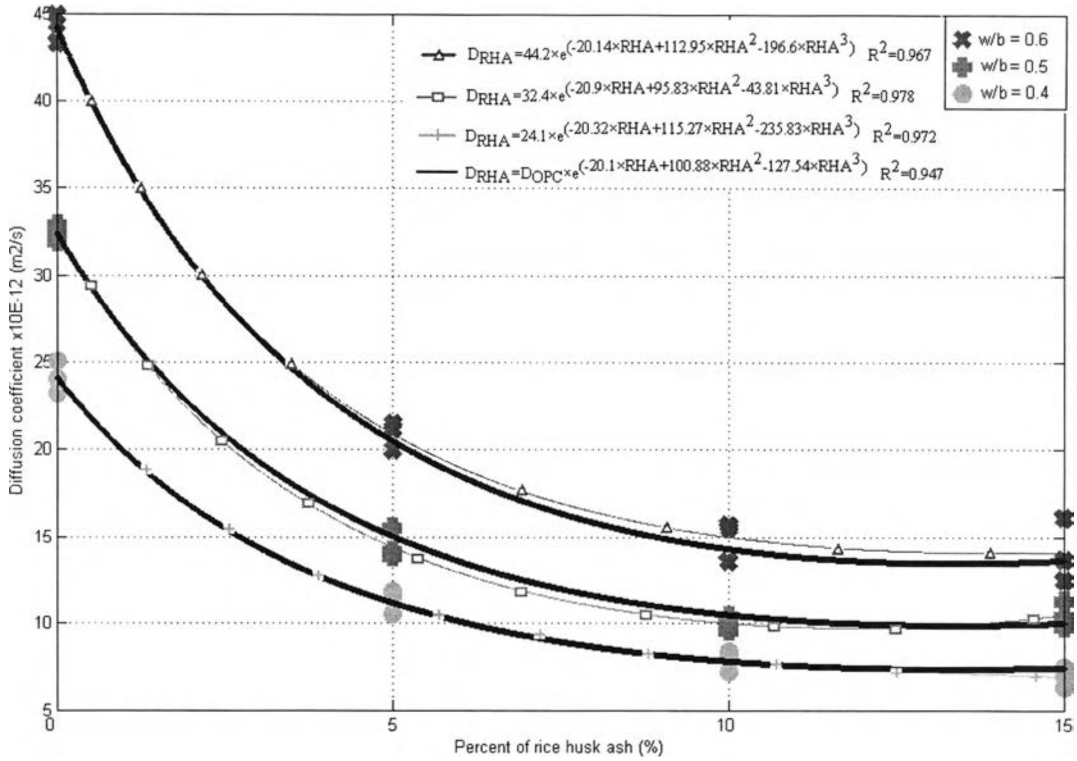


**Figure 4.10** General equation and particular equations of diffusion coefficient for different series of water binder ratio

From figure 4.10, there is not much different between these two sets of equations even with high water binder ratio of 0.6 as previous case and with high amount of rice husk ash of up to 10% and 15%. It can be explained by the extremely high pozzolanic reactivity of rice husk ash even at the early age 28 days. It means that the general equation can be applied to compute the chloride diffusion coefficient for case of partial replacement of Portland cement by rice husk ash, thank to the high pozzolanic reactivity of rice husk ash.

*4.1.2.3 Case of partial replacement by both fly ash and rice husk ash:*

As explaining earlier, fly ash has low reactivity whereas rice husk ash has high pozzolanic activity due to the high amount of silicate oxide and extreme high surface area. However, fly ash on the other hand has advantage of increase workability due to the ball bearing effect of fly ash. While rice husk ash increases cohesion and decrease segregation of cement paste. Undoubtedly, incorporate these two kinds of pozzolan will produce the mix that can take advantages of fly ash as well as rice husk ash. Table 4.7 shows the values of chloride diffusion coefficient from the experiment for this ternary blend case.

**Table 4.4** Chloride diffusion coefficient for case of triple blend

| No. | w/b | FA | RHA | Average chloride depth $X_d$ (mm) | | | Diffusion coefficient ($10^{-12}$ $m^2/s$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 1st specimen | 2nd specimen | 3rd specimen | 1st specimen | 2nd specimen | 3rd specimen |
| D.8 | 0.4 | 15 | 5 | 10.25 | 10.00 | 9.88 | 10.4 | 10.2 | 10.1 |
| D.9 | 0.4 | 15 | 10 | 6.13 | 6.75 | 6.25 | 6.0 | 6.7 | 6.1 |
| D.10 | 0.4 | 25 | 5 | 8.13 | 9.13 | 7.75 | 8.1 | 9.2 | 7.7 |
| D.11 | 0.4 | 25 | 10 | 5.13 | 4.88 | 4.25 | 5.1 | 4.8 | 4.2 |
| D.19 | 0.5 | 15 | 5 | 12.25 | 13.88 | 12.88 | 12.5 | 14.3 | 13.2 |
| D.20 | 0.5 | 15 | 10 | 9.00 | 10.75 | 10.00 | 9.0 | 10.8 | 10.1 |
| D.21 | 0.5 | 25 | 5 | 10.25 | 11.75 | 12.00 | 10.3 | 11.9 | 12.1 |
| D.22 | 0.5 | 25 | 10 | 6.75 | 7.88 | 7.13 | 6.6 | 7.7 | 7.0 |
| D.30 | 0.6 | 15 | 5 | 20.13 | 19.00 | 19.88 | 21.0 | 19.8 | 20.7 |
| D.31 | 0.6 | 15 | 10 | 13.38 | 14.75 | 14.25 | 13.5 | 15.2 | 14.4 |
| D.32 | 0.6 | 25 | 5 | 16.38 | 16.00 | 17.00 | 16.6 | 16.2 | 16.9 |
| D.33 | 0.6 | 25 | 10 | 12.00 | 9.00 | 10.00 | 12.1 | 9.0 | 10.0 |

Obviously, when investigate the ternary blend, we take into account three parameters: water binder ratio, percent of fly ash and percent of rice husk ash. The fashion of the expression of chloride diffusion coefficient for the ternary blend case is introduced as follows:

$$D_{Triple} = D_{OPC} \times k_{FA} \times k_{RHA} \times k_{FA\&RHA} \qquad (4.5)$$

Where:

$D_{Triple}$ = chloride diffusion coefficient of ternary blend case.
$D_{OPC}$ = chloride diffusion coefficient of ordinary Portland cement case, taken in account water binder ratio.
$k_{FA}$ = factor takes in account the influence of fly ash and sand content that proposed in fly ash case earlier.
$k_{RHA}$ = factor takes in account the influence of rice husk ash and sand content that proposed in rice husk ash case earlier.
$k_{FA\&\ RHA}$ = factor that takes in account the reciprocal influence between fly ash and rice husk ash.

The theoretical background of the above fashion is considering the effects ternary blend case as the reciprocal influence between fly ash case and rice husk ash case. It means that both pozzolanic reactivity of fly ash and rice husk ash are taken in account in ternary blend. Based on this theory, the expression for ternary blend case can be expressed sufficiently by only one factor $k_{FA,\ RHA}$ instead of three different factors in above fashion. However, it will be more difficult to investigate the influence of each component separately (fly ash and rice husk ash in the current case) besides their incorporate effects in the ternary blend on chloride diffusion coefficient. Furthermore, by introducing three different factors separately, we can consider the ternary blend case as the general case for both particular fly ash and rice husk ash cases. It means that we can use the data in previous fly ash and rice husk ash cases to obtain or observe the overview of chloride diffusion coefficient for pozzolan case by substitute into the above expression for ternary blend case. It will be discussed in more details at the end of this section.

Figure 4.11, 4.12 and 4.13 illustrate the relationship between chloride diffusion coefficient and water binder ratio as well as with percent of fly ash and percent of rice husk ash.

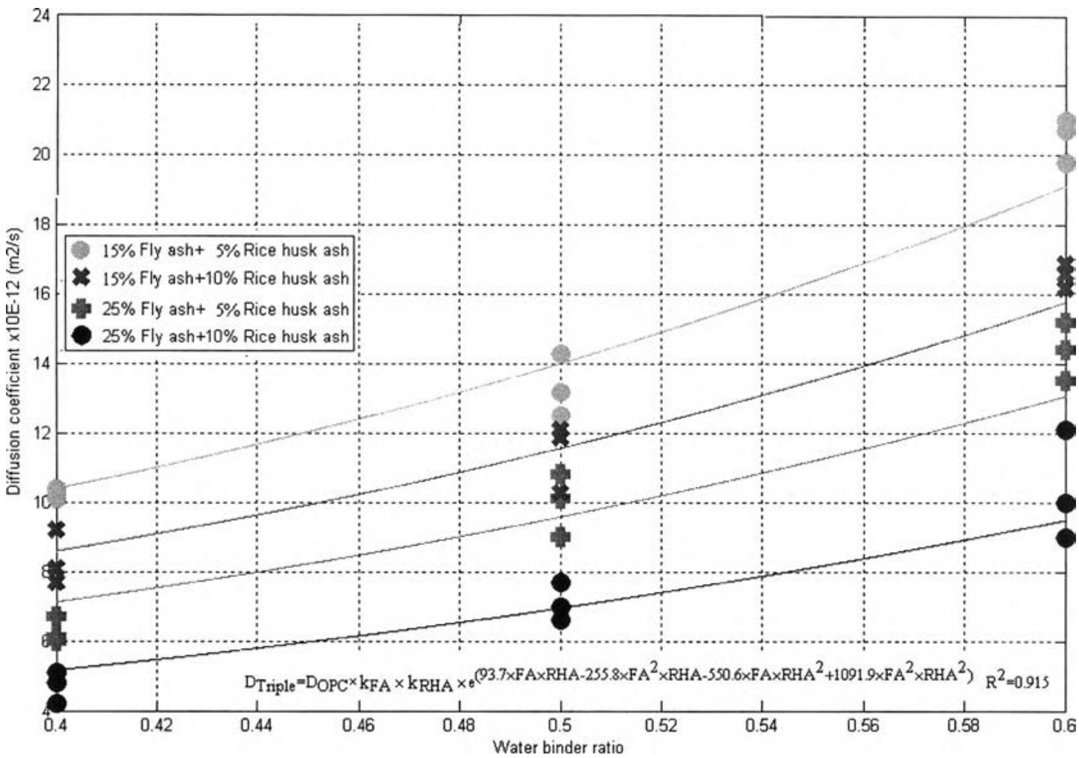


**Figure 4.11** Chloride diffusion coefficients in term of water binder ratio for ternary blend case

The values of k factors $k_{FA}$ and $k_{RHA}$ are the same as fly ash case and rice husk ash case. And the factor $k_{FA\&RHA}$ which indicates the reciprocal influence between fly ash and rice husk ash is as follows:

$$k_{FA\&RHA} = e^{\left(93.7\times FA\times RHA - 255.8\times FA^2\times RHA - 550.6\times FA\times RHA^2 + 1091.9\times FA^2\times RHA^2\right)} \tag{4.6}$$

Where:

$k_{FA\&RHA}$ = factor that takes in account the reciprocal influence between fly ash and rice husk ash.

FA = percent of fly ash.

RHA = percent of rice husk ash.

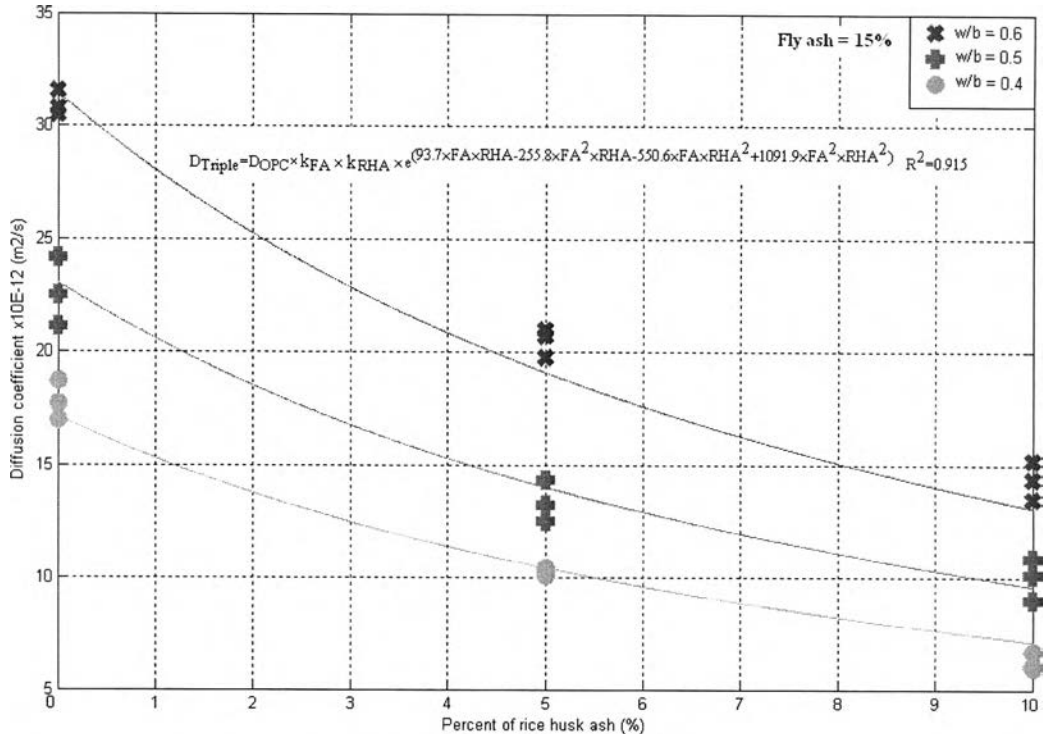


**Figure 4.12** Chloride diffusion coefficients in term of percent of rice husk ash for ternary blend case (with 15% FA)

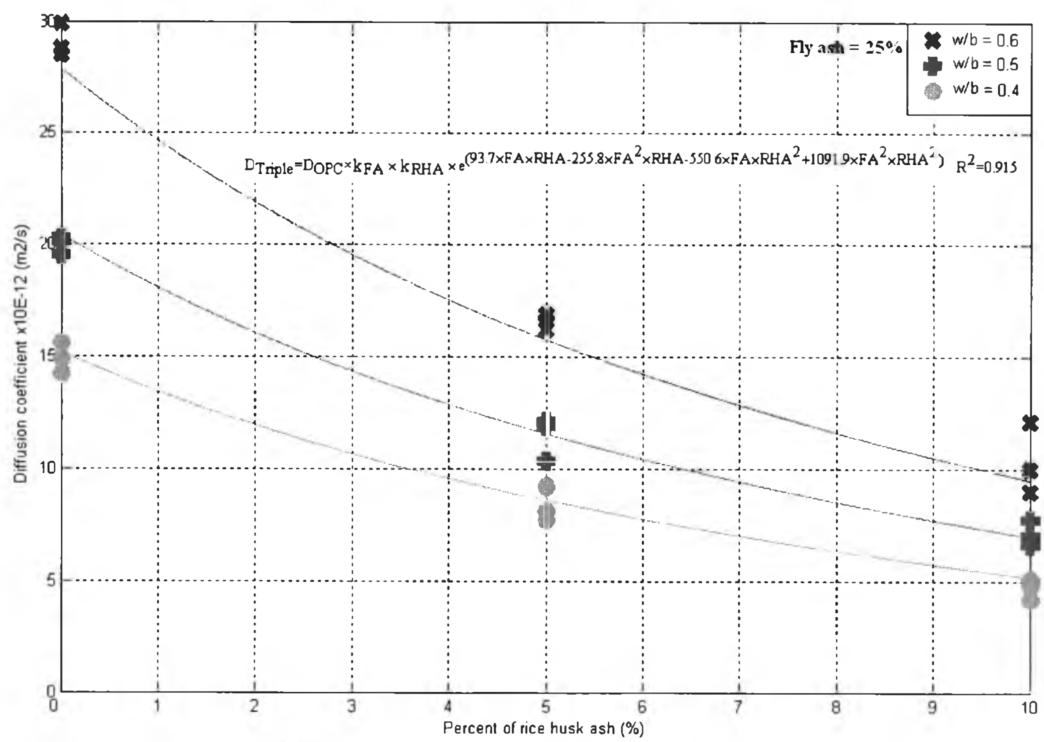


**Figure 4.13** Chloride diffusion coefficients in term of percent of rice husk ash for ternary blend case (with 25% FA)

From the above figures, it can be seen that the ternary blend has larger impact on reducing chloride diffusion coefficient than binary case, for example only fly ash case or only rice husk ash case. Figure 4.14 shows how the factor $k_{FA\&\ RHA}$ that takes in account the influence of both fly ash and rice husk ash affects the chloride diffusion coefficient based on the data of chloride diffusion coefficient with two cases of 15% and 25% fly ash and with the range of rice husk ash from 0%, 5% and 10%. The data of chloride diffusion coefficient of 0% rice husk ash and 15% fly ash and of 0% rice husk ash and 25% fly ash can be seen from the table 4.2 for only fly ash case. The data of chloride diffusion coefficient for other combination can be obtained from table 4.4 for ternary blend case.

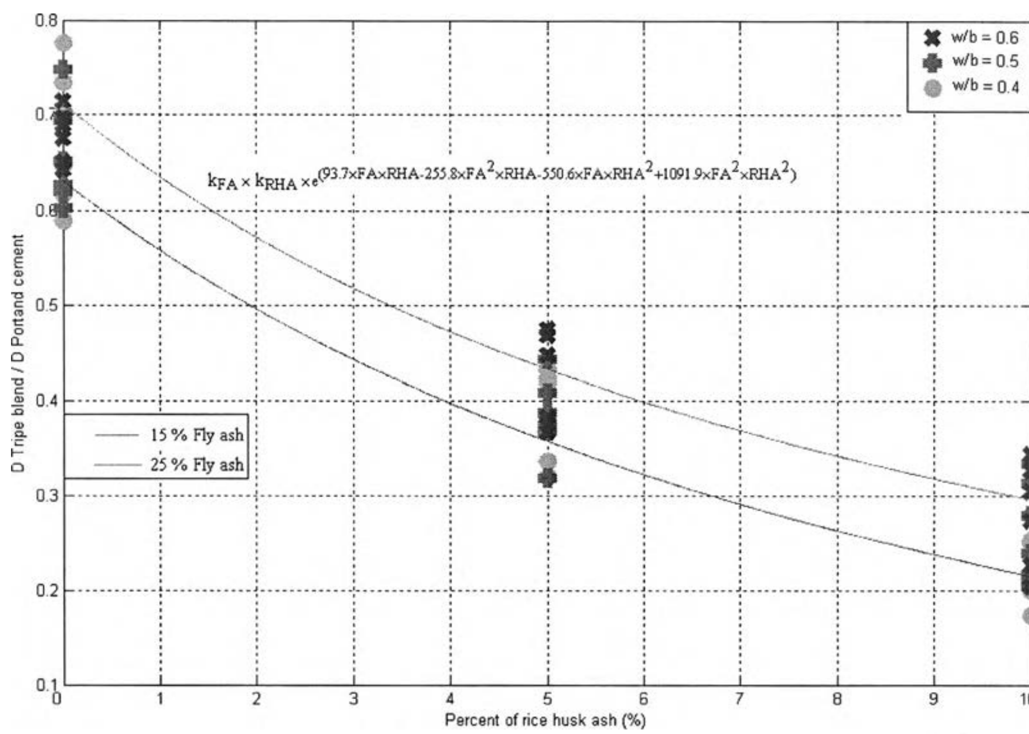


**Figure 4.14** The influence of both of fly ash and rice husk ash on chloride diffusion coefficient by factor $k_{FA\&\ RHA}$

Obviously, from figure 4.14, the order of the values of water binder ratio is in the same manner as fly ash case. It can be explained due to the appearance of fly ash component in ternary blend. With slow pozzolanic reactivity, fly ash can not react strongly like rice husk ash does at the early age 28 days. However, at the later age, for example, at 91 days, the influence of fly ash on chloride diffusion coefficient will be more significant than at early age 28 days. It means that after 91 days, the ternary blend case can take advantages of both fly ash and rice husk ash on decrease chloride diffusion coefficient. And with the same approach as previous cases in order to investigate only factor $k_{FA\&\ RHA}$ on chloride diffusion coefficient, three particular equations for each series of water binder ratio are derived and compared with the general equation for all three water binder ratio, as shown in figure 4.15 and 4.16.

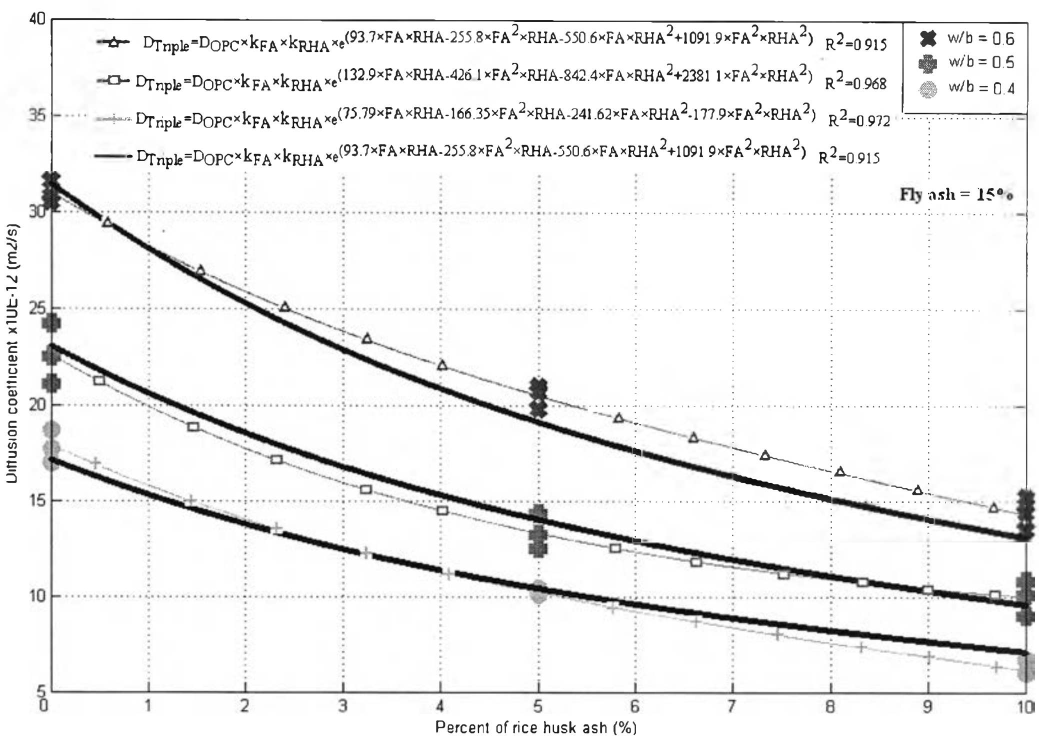


**Figure 4.15** General equation and particular equations of diffusion coefficient for different series of water binder ratio (with 15% Fly ash)

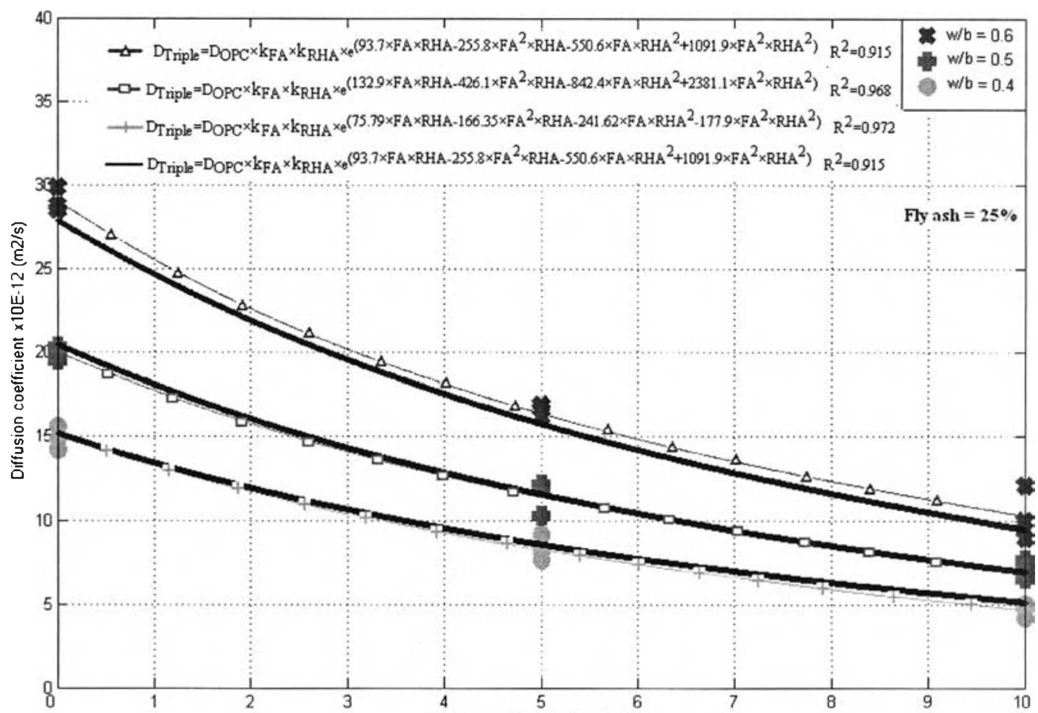


**Figure 4.16** General equation and particular equations of diffusion coefficient for different series of water binder ratio (with 25% Fly ash)

From these above figures, it can be easily seen that the general equation can be applied for the individual cases for each series of water binder ratio. However, it can be easily seen with in both figures with water binder ratio of 0.6, there is a significant different between general equation and particular expression. It means that with high water binder ratio of 0.6, there should be careful when employing the general equation for the application. The reason is with high water binder ratio of 0.6, the pozzolanic reactivity of fly ash is slower than usual. This phenomenon with high water binder ratio of 0.6 is in correlation with the behavior of fly ash in only fly ash case. However, in the current case, it occurs even with small amount of fly ash, about 15% and 25%, in compared with the previous only fly ash case, about 25% and 35%. It can be explained by the participation of rice husk ash in ternary blend. Therefore, it can concluded that in ternary blend at the high water binder ratio of 0.6, the pozzolanic reactivity of fly ash will be decreased than usual with even small amount of fly ash due to the participation of rice husk ash.

In conclusion, this general equation can be applied for all four particular cases: ordinary Portland cement case, binary blend cases with partial replacement of Portland cement by fly ash or rice husk ash and ternary blend case with reciprocal influence between fly ash and rice husk ash, however when employing with high water binder ratio of 0.6 we should pay attention and be careful.

Finally, in order to present the chloride diffusion coefficient in a visual manner, plots with contours are performed, as shown in figure 4.17, 4.18 and 4.19. By the visual manner, these contours obviously can illustrate the overview of the fluctuation of chloride diffusion coefficient in accordance with percent of fly ash and rice husk ash. This is the most important usefulness of these contours. Furthermore, from observing these contours, some extensions of application of the proposed expression of chloride diffusion coefficient can be drawn out.

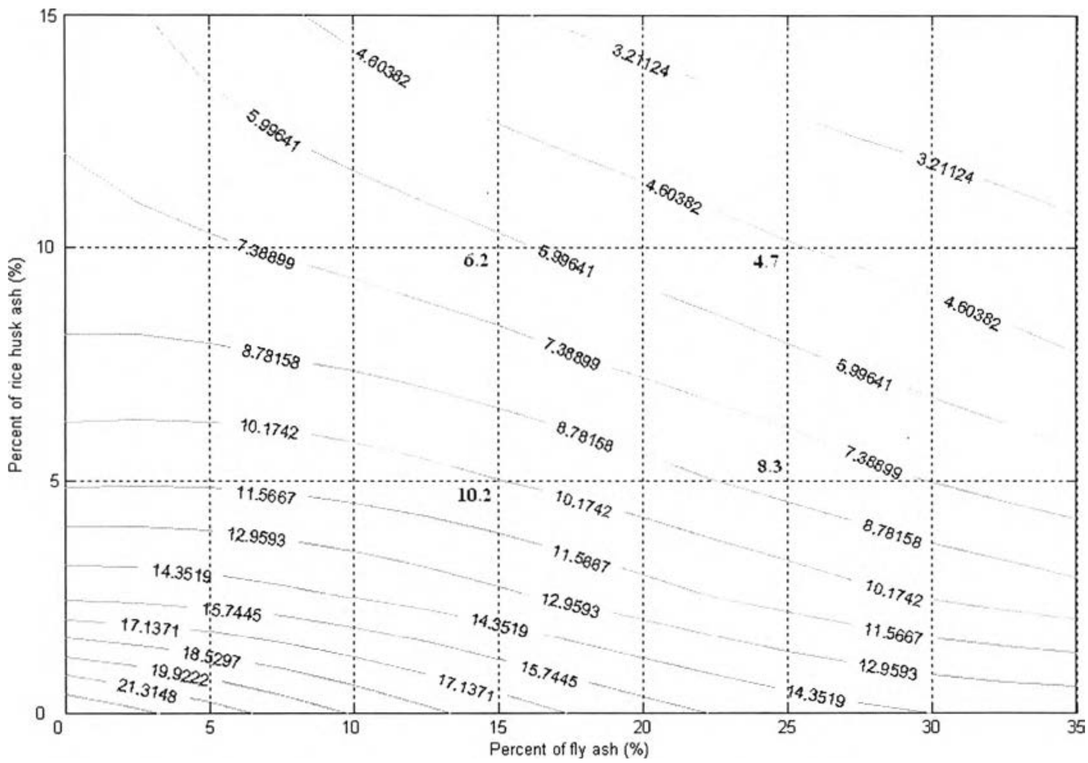


**Figure 4.17** Contour of chloride diffusion coefficient with water binder ratio 0.4

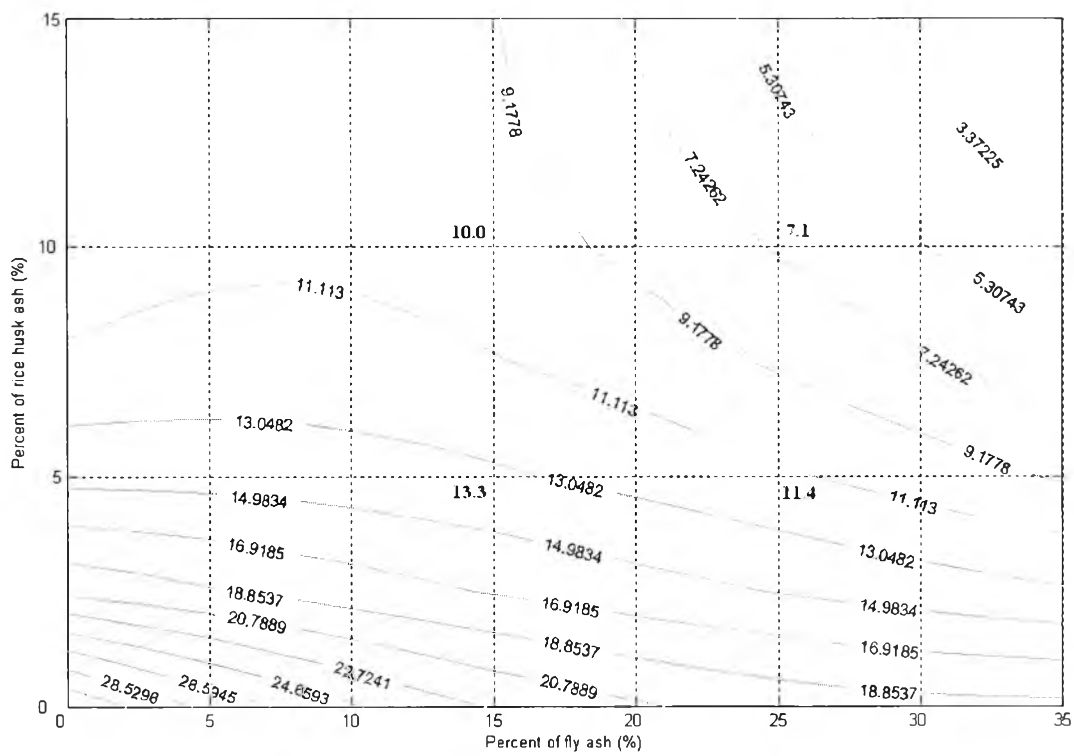


**Figure 4.18** Contour of chloride diffusion coefficient with water binder ratio 0.5

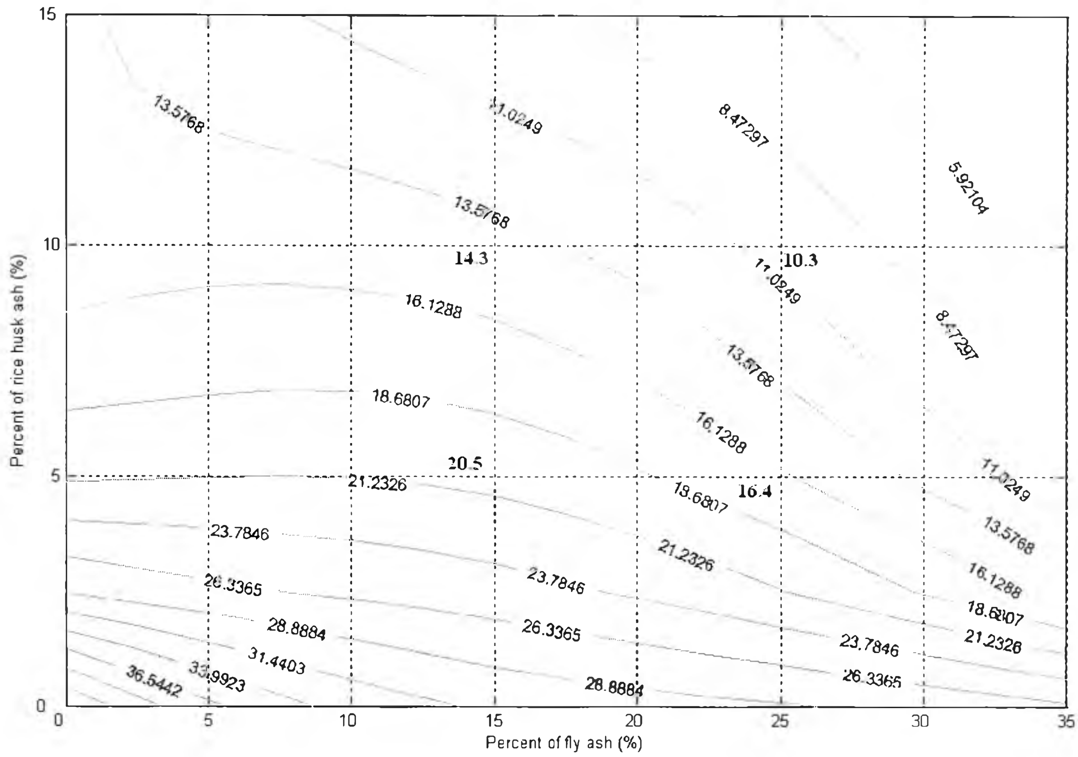


**Figure 4.19** Contour of chloride diffusion coefficient with water binder ratio 0.6

Generally speaking, it can be drawn out from these above figures that at the early age 28 days (for the current study) obviously only rice husk ash affects the chloride diffusion coefficient and the effect of fly ash is not much significant. However, at the later age, for example after 91 days, the chloride diffusion coefficient will decrease as the pozzolanic reactivity of fly ash shows its effect. It means that at 91 days, both fly ash and rice husk ash have remarkable influence on decrease the chloride diffusion coefficient.

Furthermore, from these above contours, the chloride diffusion coefficient decreases with the increase of amount of fly ash as well as the increase of amount of rice husk ash. The minimum value of chloride diffusion coefficient can be obtained with water binder ratio 0.4 and 35% percent of fly ash plus 15% of rice husk ash. In addition, obviously the same chloride diffusion coefficient can be achieved with different proportion amount of fly ash and rice husk ash. Based on this observation, some extensions of application of ternary blend can be drawn. First of all, if we consider the chloride ingress associating with the sulfate attack, the amount of fly ash should be reduced as much as possible due to the high amount of aluminum oxide content in fly ash composition. In order to understand clearer about this matter, we should take a quick look at mechanism of sulfate attack. Basically, sulfate attack starts with penetration of sulfate ions into the cement paste. After that, two detrimental reactions will occur as follows:

$$Ca(OH)_2 + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.H_2O + 2OH^- \qquad (4.7)$$

$$C_3A + 3CaSO_4 + 32H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O \quad (4.8)$$

The formation of ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) causes the expansion which then leads to cracking of concrete structures.

Another reason for reducing amount of fly ash should be considered when the freezing and thawing attack is included besides the chloride ingress. This can be investigated by the amount of carbon content in fly ash which is related to the ability of maintaining a stable air void system, in turn, relates to the resistance to freezing and thawing attack. It means that the higher amount of carbon content is the more vulnerable of concrete structure to freezing and thawing attack is. The carbon content of fly ash is often given by the loss of ignition value (LOI). Normally, it is recommended that the air content of the concrete should be measured regularly when using a fly ash with LOI value greater than 3 percent.

In addition, fly ash containing high concentrations of sulfur, as measured by $SO_3$, should be checked for the potential for efflorescence when considering the amount of fly ash in ternary blend. Although efflorescence is not a structural concern, it may cause problems in architectural products.

Finally, the amount of fly ash should be reduced when using fly ash that contains calcium oxide CaO in the form of free lime, especially in low water binder ratio mixes. Because if there is not enough moisture present to hydrate the free lime prior to initial set, delayed hydration may cause detrimental volume changes.

On the other hand, the amount of rice husk ash should be considered when the designed strength is included besides the resistance to chloride ingress. Because, the high amount of rice husk ash, more than 10 percent may cause the loss of strength significantly at the later age (Gemma Rodriguez de Sensale 2005)

At last, the require additional storage bins or silos should be also considered when using ternary blend because in this case, it can not use the same silos for all three kinds of Portland cement, fly ash and rice husk ash. However, the money saved by reducing the amount required cement can compensate.

**4.2 Experiments with real sea water:**

The objectives of the experiments with real sea water are to verify the data of chloride diffusion coefficient from the experiments with simulated solution and on the other hand to observe if there is any strange phenomenon happen between these two cases. Because it is known that the composition of sea water is more complicated with containing many kinds of chemical components than the simulated solution with containing only chloride ions, an observation is necessary to be made in order to investigate whether there is any effects come from the other chemical component or not.

This information is very useful for the application of the proposed expressions of chloride diffusion coefficient in practice with the real sea water condition.

In the current experiments with real sea water solution, only selected cases are tested due to a large amount of specimens and the requirement of huge amount of necessary sea water. And the selected cases are ordinary Portland cement with water binder ratio 0.5 (O.1 and O.2), 25 percent of partial replacement of Portland cement by fly ash with water binder 0.5 (F.1 and F.2), 10 percent of partial replacement of Portland cement by rice husk ash with water binder ratio 0.5 (R.1 and R.2) and triple blend case with 25 percent fly ash, 10 percent rice husk ash and water binder ratio 0.5 (T.1 and T.2). The reasons for selecting the above cases is that water binder ratio of 0.5, 25 percent of fly ash and 10 percent of rice husk ash are more common cases in practice. The results with these selected cases collected from the experiments with real sea water can be seen from the table 4.5 and 4.6. Moreover, table 4.7 also presents the composition of sea water taken from Cha-Am, Gulf of Thailand and Ca Na, Vietnam which are analyzed by Chulalongkorn University and Ho Chi Minh University of Technology, respectively.

**Table 4.5** Chloride diffusion coefficient for the experiments with real sea water taken from Cha- Am, Gulf of Thailand

| **No.** | **Average chloride depth $X_d$ (mm)** | | | **$X_d$ average (mm)** | **$D_{average}$ $10^{-12}$ $m^2/s$** | **$D_{average}$ $10^{-12}$ $m^2/s$ (simulated condition)** | **Δ (%)** |
|---|---|---|---|---|---|---|---|
| | **1$^{st}$ specimen** | **2$^{nd}$ specimen** | **3$^{rd}$ specimen** | | | | |
| O.1 | 28.13 | 27.88 | 30.50 | 28.84 | 29.9 | 32.4 | 8 |
| F.1 | 17.25 | 18.38 | 17.50 | 17.71 | 17.9 | 20.0 | 11 |
| R.1 | 10.50 | 12.50 | 10.00 | 11.00 | 11.2 | 10.0 | 12 |
| T.1 | 7.88 | 6.13 | 6.25 | 6.75 | 6.4 | 7.1 | 10 |

**Table 4.6** Chloride diffusion coefficient for the experiments with real sea water taken from Ca Na, Vietnam

| **No.** | **Average chloride depth $X_d$ (mm)** | | | **$X_d$ average (mm)** | **$D_{average}$ $10^{-12}$ $m^2/s$** | **$D_{average}$ $10^{-12}$ $m^2/s$ (simulated condition)** | **Δ (%)** |
|---|---|---|---|---|---|---|---|
| | **1$^{st}$ specimen** | **2$^{nd}$ specimen** | **3$^{rd}$ specimen** | | | | |
| O.2 | 28.50 | 29.13 | 30.25 | 29.29 | 30.1 | 32.4 | 7 |
| F.2 | 18.38 | 18.88 | 19.00 | 18.75 | 18.8 | 20.0 | 6 |
| R.2 | 9.50 | 8.13 | 10.25 | 9.29 | 9.1 | 10.0 | 9 |
| T.2 | 7.50 | 6.25 | 6.13 | 6.23 | 6.3 | 7.1 | 11 |

**Table 4.7** Composition of sea water taken from Cha-Am, Gulf of Thailand and Ca Na, Vietnam.

| Composition | Content (mg/l) | |
|---|---|---|
| | Cha-Am (Thailand Gulf) | Ca Na (Vietnam) |
| NaCl | 24,926 | 27,444 |
| $MgCl_2$ | 2,481 | 3,118 |
| $MgSO_4$ | 2,467 | 2,412 |
| $CaSO_4$ | 875 | 674 |

The above data is well in accordance with results obtained from previous experiments with simulated condition. Generally speaking, most of chloride diffusion coefficients testing with real sea water are slightly smaller than testing with simulated catholyte solution. This can be explained due to the decrease in chloride concentration. However, obviously testing with simulated catholyte solution is on the safe side.

On the other hand, there are some strange phenomenon occurred, comparing with previous experiments. First of all, the color of catholyte solution becomes muddy with time. Secondly, after spray the silver nitrate on the splitting surface, the color of chloride penetration depth is obviously darker. This can be explained due to the appearance of sulfate $SO_4^{2-}$ ion, $CO_3^{2-}$ and $PO_4^{3-}$ in the catholyte solution. These ions move into the concrete specimen, react with silver nitrate, and finally precipitates are formed. All of these kinds of precipitates make the color of penetration depth become darker.

### 4.3 Empirical expressions:

As discuss in first section of this chapter, the current work proposes four expressions for predicting the chloride diffusion coefficient in term of water binder ratio, percent of partial replacement of Portland cement by fly ash and percent of partial replacement of Portland cement by rice husk ash. However, when apply the equation for fly ash case with higher water binder ratio 0.6 and large amount of fly ash 25% and 35%, we should pay more attention. Furthermore, in ternary blend case, it should also be more careful when applying the equation with high water binder ratio of 0.6. In addition, these equations are only used for case of partial replacement of Portland cement, not for case of adding pozzolan. Finally, these expressions are as follows:

- For ordinary Portland cement case:

$$D_{opc} = 25.28 - 71.98\times(w/b) + 172.5\times(w/b)^2 \qquad (4.9)$$

- For case of adding fly ash:

$$D_{FA} = D_{opc} \times e^{\left(-3.02\times FA + 5.53\times FA^2 - 3.24\times FA^3\right)} \qquad (4.10)$$

- For case of adding rice husk ash:

$$D_{RHA} = D_{opc} \times e^{\left(-20.1\times RHA + 100.88\times RHA^{2} - 127.54\times RHA^{3}\right)} \quad (4.11)$$

- For case of triple blend:

$$D_{Triple} = D_{opc} \times k_{FA} \times k_{RHA} \times e^{\left(93.7\times RHA\times FA - 255.8\times RHA\times FA^{2} - 550.6\times RHA^{2}\times FA + 1091.9\times RHA^{2}\times FA^{2}\right)} \quad (4.12)$$

Where:

D = Chloride diffusion coefficient.
w/b = Water binder ratio.
FA = Percent of partial replacement of Portland cement by fly ash.
RHA = Percent of partial replacement of Portland cement by rice husk ash
$k_{FA}$ = Factor that takes in account the influence of fly ash and sand content
$= e^{\left(-3.02\times FA + 5.53\times FA^{2} - 3.24\times FA^{3}\right)}$
$k_{RHA}$ = Factor that takes in account the influence of rice husk ash and sand content
$= e^{\left(-20.1\times RHA + 100.88\times RHA^{2} - 127.54\times RHA^{3}\right)}$