Design of Experiment

Final Project

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PART 01

Literature Review

Abstract

- "Experimental correlation using ANOVA and DOE studies on corrosion behavior of Fe and Ni-based alloy under different media"

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- Used DOE and ANOVA to evaluate the effect of temperature, immerse time, and different corrosive media such as HCL, H_2SO_4 and KOH at different time intervals at 30°C, 40°C and 60°C on the corrosion behavior of Fe and Ni-based alloy.

Experiment method

- The experimental works were done on four based alloys.

- First, they were washed with tap water and with double distilled water, dried in air and then washed with acetone. Dried in hot air and weighed on an analytical balance to accuracy.

- The specimen weights were noted and then dipped into the test solution at different temperatures 30 $^{\circ}$C, 40 $^{\circ}$C and 60 $^{\circ}$C. At regular time intervals up to 30 min, the specimen was removed from the test solution and washed with tap, double distilled water, dried in the air, washed with acetone and again dried in hot air. Finally, the weights registered after 200 min.

- The differences in weights at each interval were observed and the corrosion rates and specific reaction rates were measured.

Analysis

The levels of different factors studied are %Ni eq., (17.7%–99.9%), %Cr eq., (0%–39.2%), temperature (30 °C, 40 °C and 60 °C), time intervals (30–200) and pH value of different corrosive media (such as HCL, H_2SO_4 and KOH at 1.01, 2.08, and 12.8, respectively).

Table 1. The chemical composition of Fe and Ni-based alloy.

		Chemical composition, %								
	Alloy code	Ni	Cr	Mo	Fe	Si	Mn	Al	Ti	Nb
1	Ni-24Cr-10Mo	65.40	24.40	9.87	0.00	0.00	0.00	0.00	0.00	0.00
2	Ni pure	99.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	Fe-35Ni-22Cr	35.20	21.90	0.00	40.70	0.58	0.94	0.13	0.32	0.05
4	Fe-17Ni-18Cr	17.00	17.70	1.26	60.90	0.35	1.45	0.01	0.00	0.75

$$\%Ni\ eq. = \%Ni + \%Co + 30(\%C) + 25(\%N) + 0.5(\%Mn) + 0.3(\%Cu)$$

$$\%Cr\ eq. = \%Cr + 2\%Si + 1.5(\%Mo) + 5(\%V) + 5.5(\%Al) + 1.75(\%Nb) + 1.5(\%Ti) + 0.75(\%W)$$

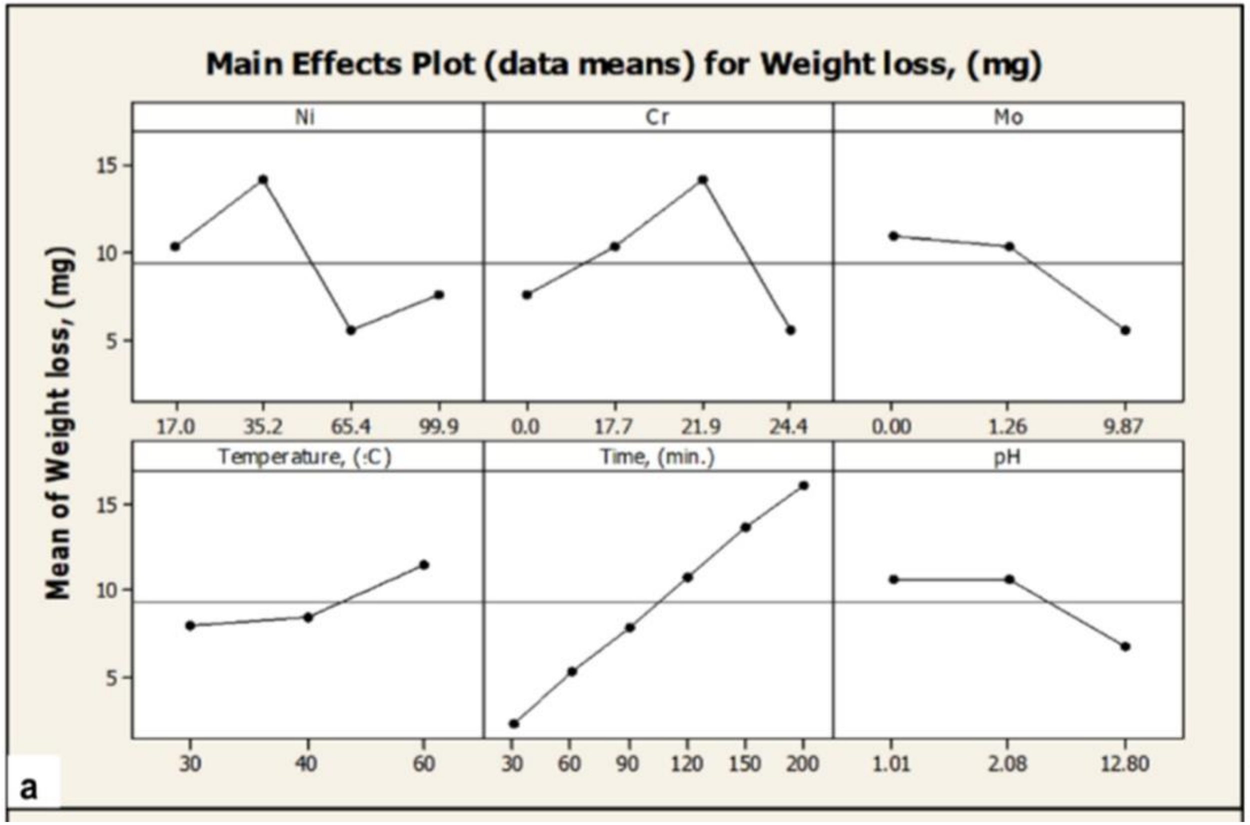
Table 2. Design of experiment (DOE) factors and their uncoded levels.

				Level			
				uncoded		coded	
No.	Parameters	Notation	Unit	Low	High	Low	High
1	% Ni eq.	A	wt%	17.7	99.9	−1	+1
2	%Cr eq.	B	wt%	0	39.2	−1	+1
3	Temperature	C	(°C)	30	60	−1	+1
4	Time	D	(min.)mm^2	30	200	−1	+1
5	pH	E	#	1.01	12.8	−1	+1

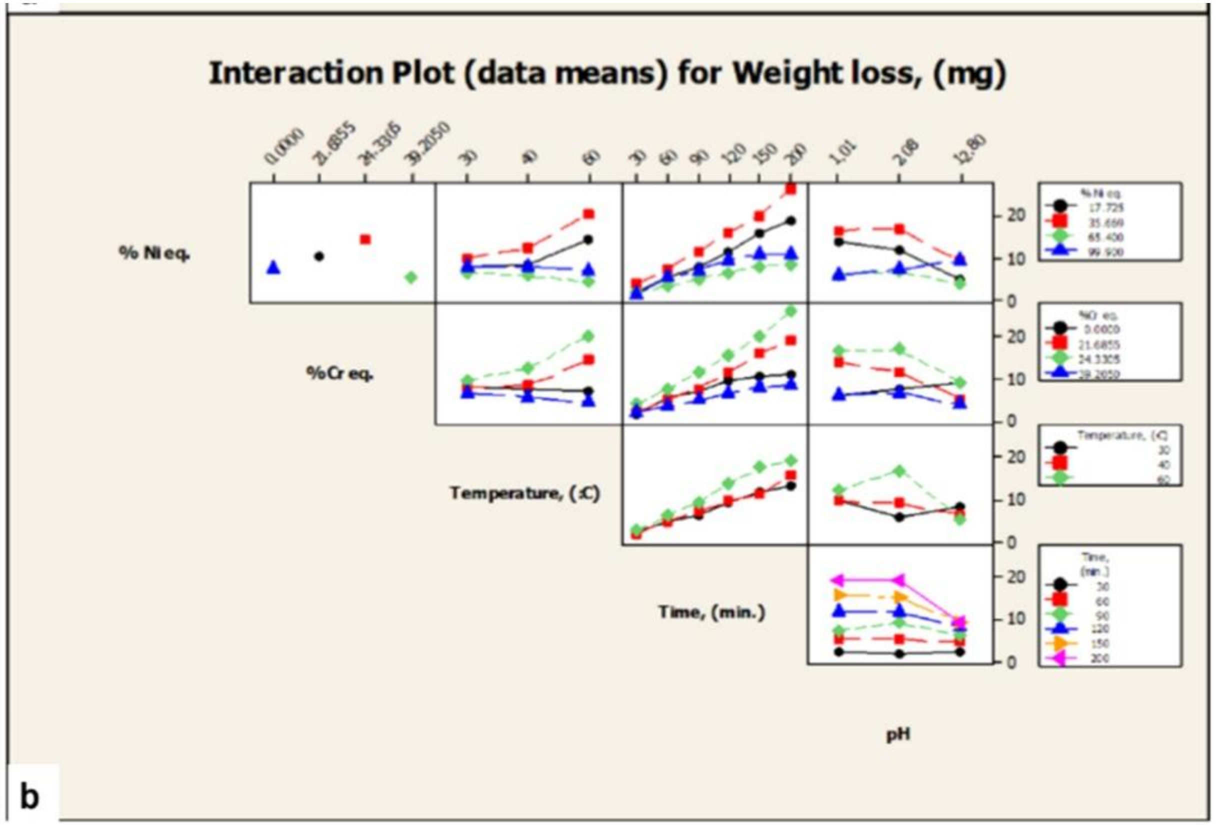
The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) are used to investigate the corroded surfaces of the alloys.

Analysis

Main effect plot for weight loss, (mg)



Interaction plot for weight loss, (mg)

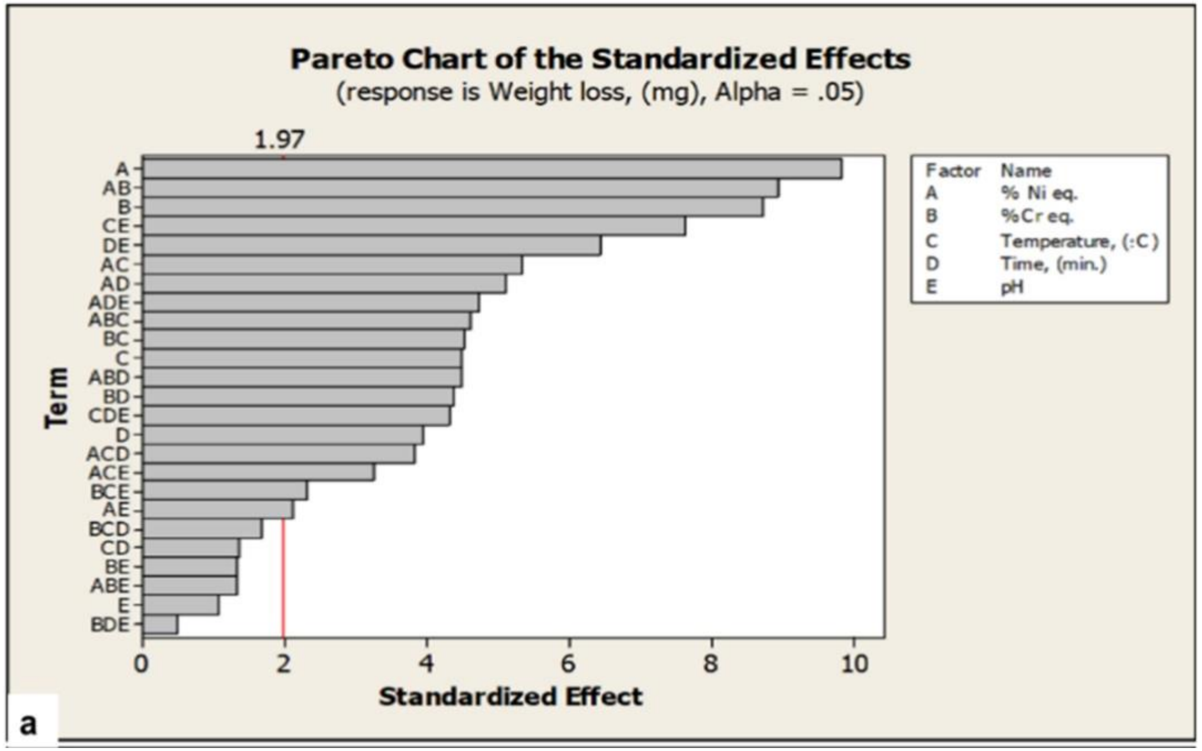


Increasing the temperature or time increases the weight loss, (mg) while increasing the %Ni eq., %Cr eq. and pH reduces the weight loss, (mg).

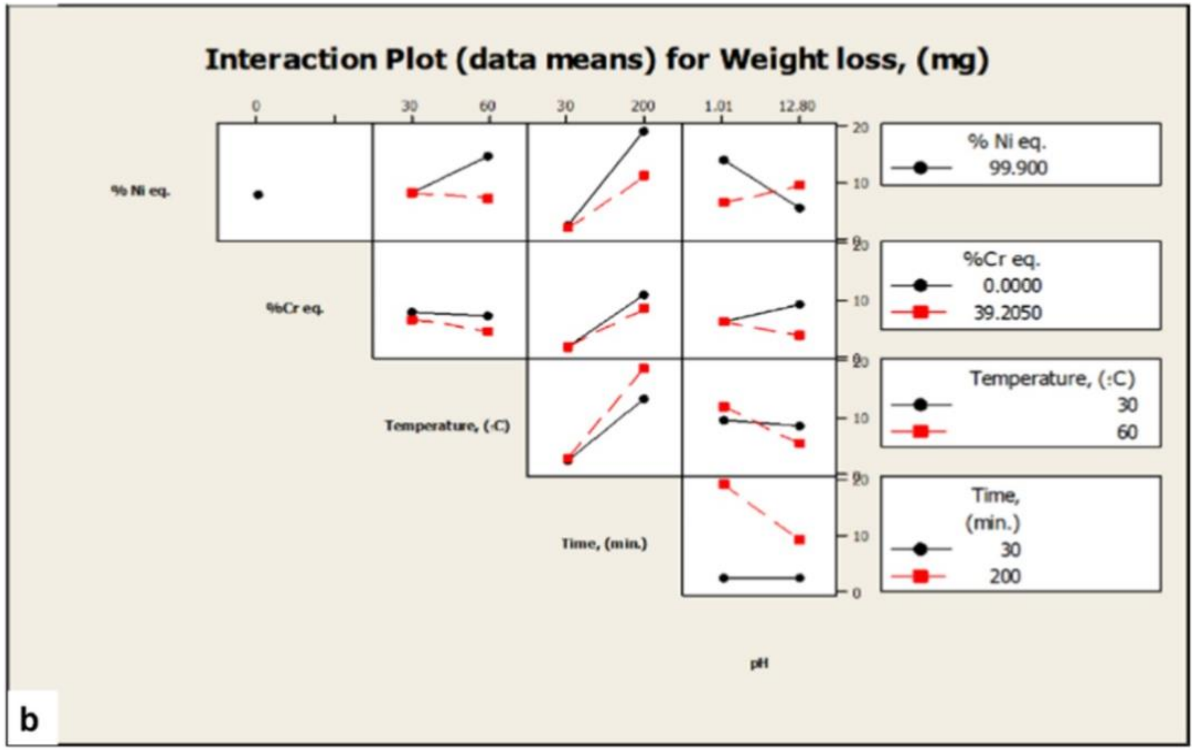
The effect of temperature or time on increasing the weight loss, (mg), is reduced as the pH increases.

Analysis

The normal probability plot of the standardized effects for weight loss, (mg)



The interaction effect plot for the mean values of weight loss, (mg)



From the chart of standardized effect, we can know which factor has the largest effect.

The interaction of %Ni eq. and pH is significant. Similarly, the interaction of temperature and pH is significant. Soaking in strong acid for a long time loses more weight than soaking in strong alkali.

Analysis

Table 3. Mathematical model (1) for weight loss, (mg): estimated coefficients for weight loss, (mg) using data in uncoded units.

Term	Coefficient	P-Value
Constant	654.721	0.000
% Ni eq.	−6.522 33	0.000
%Cr eq.	−32.1763	0.000
Temperature, (°C)	−16.7219	0.000
Time, (min)	−3.671 35	0.000
pH	13.5383	0.287
% Ni eq.*%Cr eq.	0.405 682	0.000
% Ni eq.*Temperature, (°C)	0.166 774	0.000
% Ni eq.*Time, (min)	0.036 6907	0.000
% Ni eq.*pH	−0.137 150	0.035
%Cr eq.*Temperature, (°C)	0.816 093	0.000
%Cr eq.*Time, (min)	0.177 147	0.000
Temperature, (°C)*pH	−0.035 3877	0.000
Time, (min)*pH	−0.001 565 00	0.000
% Ni eq.*%Cr eq.*Temperature, (°C)	−0.010 2688	0.000
% Ni eq.*%Cr eq.*Time, (min)	−0.002 210 10	0.000
% Ni eq.*Temperature, (°C)* Time, (min)	−4.85929E-05	0.000
% Ni eq.*Temperature, (°C)*pH	0.000 437 848	0.001
% Ni eq.*Time, (min)*pH	0.000 140 598	0.000
%Cr eq.*Temperature, (°C)*pH	0.000 694 467	0.021
Temperature, (°C)*Time, (min)*pH	−2.81753E-04	0.000

Table 4. Mathematical model (2) for corrosion rate (mg cm^{-2} h^{-1}): estimated coefficients for corrosion rate (mg cm^{-2} h^{-1}) using data in uncoded units.

Term	Coefficient	P-Value
Constant	47.8638	0.003
% Ni eq.	−0.480 393	0.001
%Cr eq.	−2.364 98	0.009
Temperature, (°C)	−0.576 647	0.368
pH	0.013 80	0.88
% Ni eq.*%Cr eq.	0.029 7176	0.042
Temperature, (°C)*pH	−0.008 436 45	0.000
% Ni eq.*Temperature, (°C)*pH	−8.67521E-05	0.002
%Cr eq.*Temperature, (°C)*pH	0.000 293 596	0.000

The R^2 and adjusted R^2 values for the weight loss, (mg) regression models are 84.53% and 82.5%, respectively. The R^2 and adjusted R^2 values for the corrosion rate (mg cm−2 h−1) regression model are 84.95% and 82.97%, respectively.

Conclusion

- Regressions models acquire an understanding of the effects of these parameters and their interactions on the weight loss, (mg) and corrosion resistance of Fe and Ni-based alloys.

- The Ni-based alloy which contains Ni-Cr-Mo is resistant to H_2SO_4 and KOH in a moderately broad range of concentrations and temperatures, whereas pure Ni is generally unsuitable for hydrochloric acid service.

- Weight loss increases with an increase in immersion time in acids and base environments. The corrosion rate increases with an increase in temperature. The corrosion rate in different environment follows the order HCL > H_2SO_4 > KOH.

Conclusion

- The effect of temperature at a constant acid concentration as in the case of HCL solutions has a strong influence on the corrosion rate of pure Ni, however, the corrosion rate of Ni-based alloy is almost unaffected by the temperature (low activation energy).

- Ni-Cr alloys show good corrosion resistance at low pH values, such as HCL. Nonetheless, Ni-Cr-Mo alloys show better corrosion resistance than Ni-Cr alloys at the higher acid concentrations, such as H_2SO_4.

PART 02

BOMB!!!

Abstract

- Baking soda and citric acid reacts to produce carbon dioxide gas. If the reaction is in the zipper bag, the carbon dioxide gas fills the room and eventually makes the bag explode.

$$3NaHCO_3 + C_6H_8O_7 \rightarrow C_6H_5Na_3O_7 + 3CO_2 + 3H_2O$$

- Test different variations and compare the explosion.
  - Grams of baking soda and citric acid
  - The volume of water
  - Whether to shake the bag or not

DOE

- Factors:

Grams of baking soda and citric acid	Volume of water added	Whether to shake the bag or not
• 2.5 g baking soda with 2.5 g citric acid • 5 g baking soda with 5 g citric acid	• 2.5 ml • 5 ml • 7.5 ml	• Shake it • Don't shake it

- Experimental unit: the zipper bags
- Response: the explosion time of each zipper bag

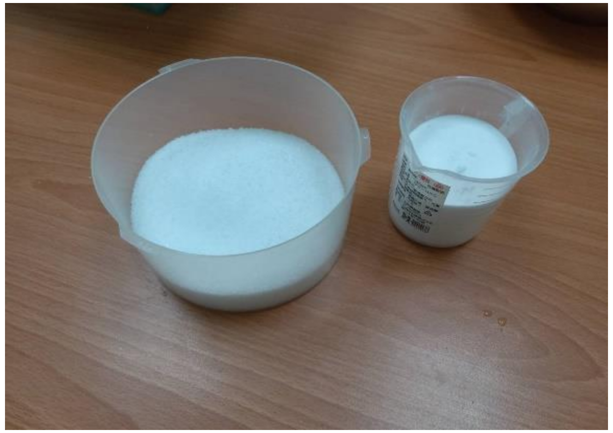
Procedure

1. Put baking soda and citric acid into the zipper bag.

2. Add water into the zipper bag.
Start the watch.

3. (Shake the bag.)
Put the bag in the fish jar and observe.
Stop the watch as the bag explode.

Equipment



Baking soda
Citric acid

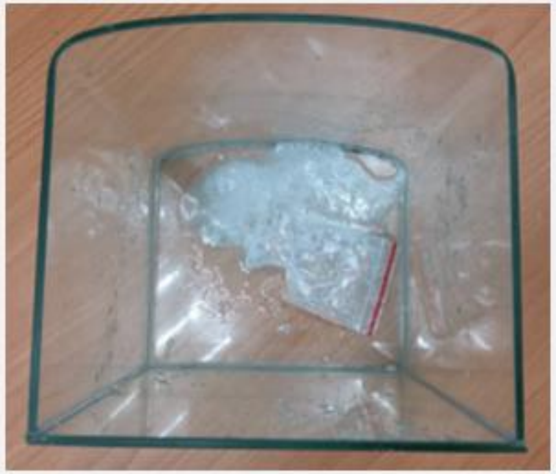
Zipper bag

Beaker
Dropper

Fish jar

Stop watch

Photos & Video

Unexploded zipper bag	Exploded zipper bag
	

Results

- Each factor-level combination has 3 replicates.

Unit: seconds

Whether to shake or not	Volume of water added	Grams of baking soda and citric acid					
		2.5 g baking soda with 2.5 g citric acid			5 g baking soda with 5 g citric acid		
No	2.5 ml	X	X	X	X	X	X
Yes		X	4.85	X	4.57	2.49	3.22
No	5 ml	X	X	4.39	X	7.93	9.83
Yes		7.16	4.40	3.80	3.34	2.28	2.41
No	7.5 ml	X	2.82	2.50	2.81	1.58	2.17
Yes		3.41	1.83	3.61	2.23	2.10	2.42

Note. "X" means the zipper bag did not explode.

Data interpretation

- Assume “X” to be 60 seconds.
- We will not take the log transformation to the data. The unexploded data will be too close to the exploded data after the transformation. This may go against the original data.

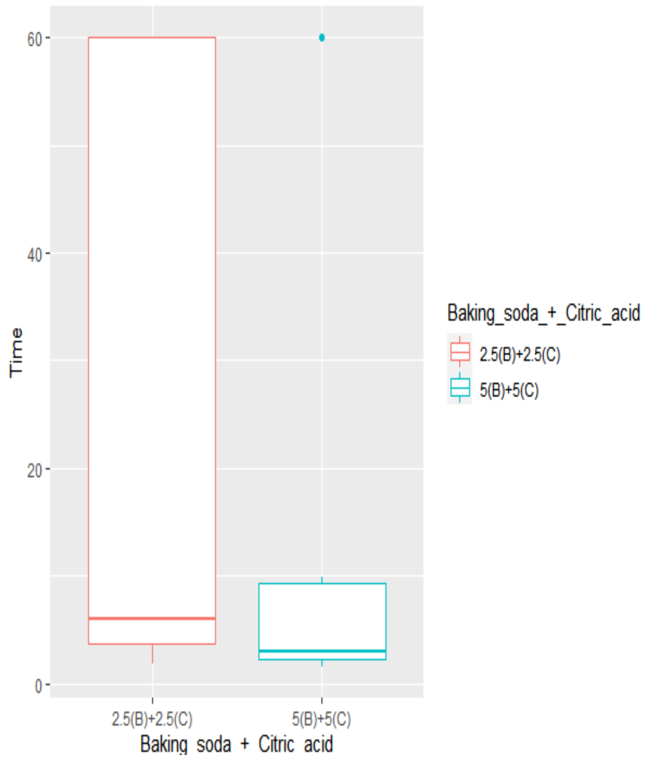
Descriptive statistics

Grams of baking soda and citric acid	
2.5 g baking soda with 2.5 g citric acid	5 g baking soda with 5 g citric acid
$\overline{\mathbf{Y}_{1..}}$	$\overline{Y_{2..}}$
28.821	16.077

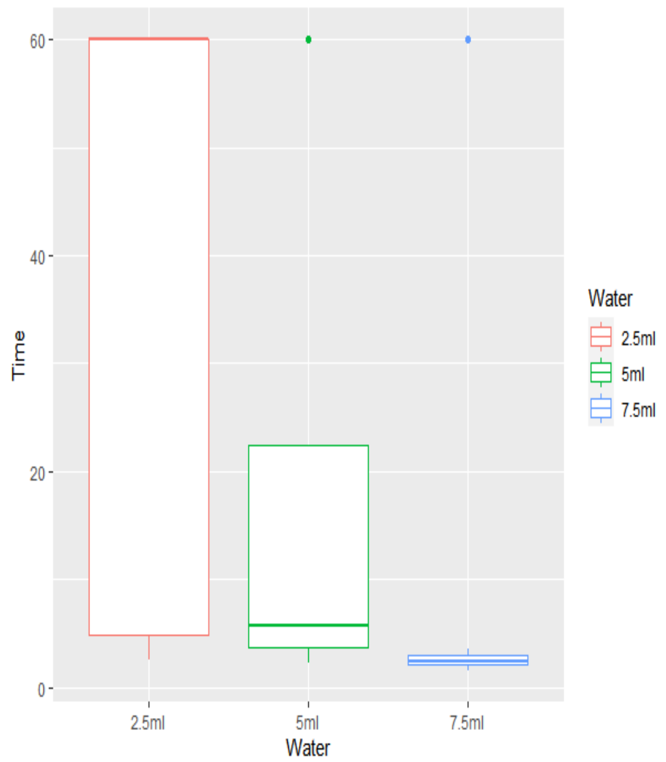
Volume of water added		
2.5 ml	5 ml	7.5 ml
$\overline{\mathbf{Y}_{.1.}}$	$\overline{Y_{.2.}}$	$\overline{Y_{.3.}}$
41.261	18.795	7.290

Whether to shake or not	
No	Yes
$\overline{\mathbf{Y}_{..1}}$	$\overline{Y_{..2}}$
35.224	9.673

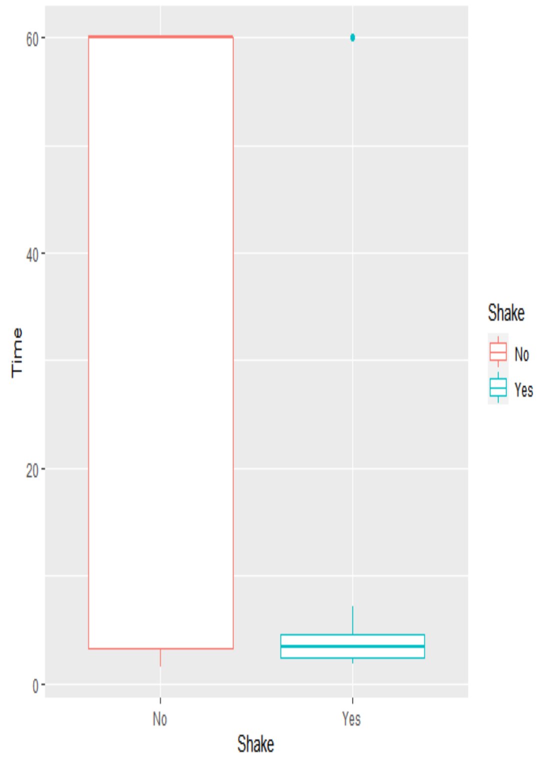
Boxplot



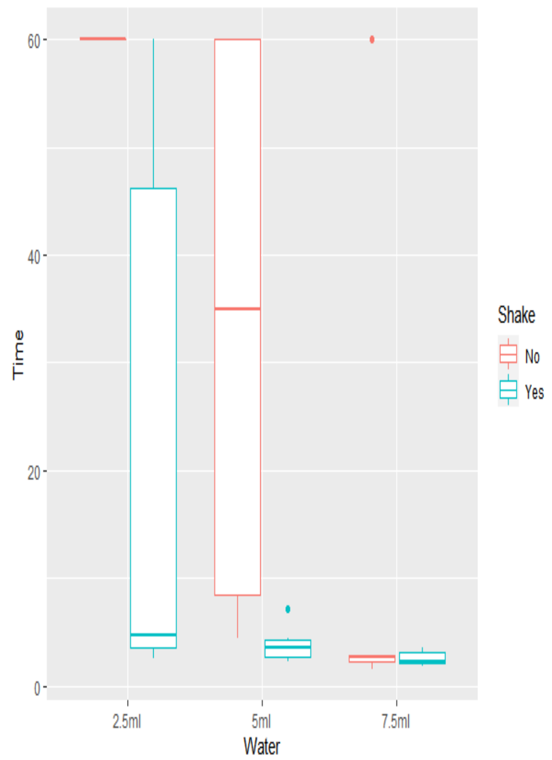
The variance of (2.5, 2.5) is larger than that of (5, 5)



7.5 ml is significantly different from the other two levels.

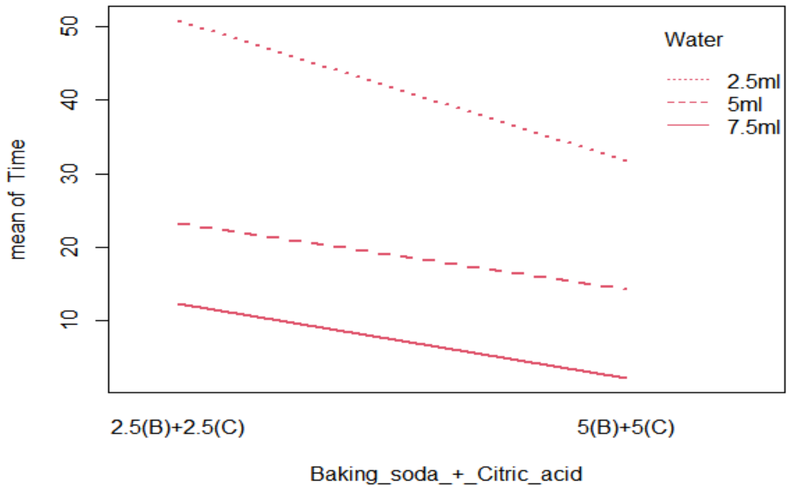


More than half of the zipper bags did not explode if not shaking the bag.

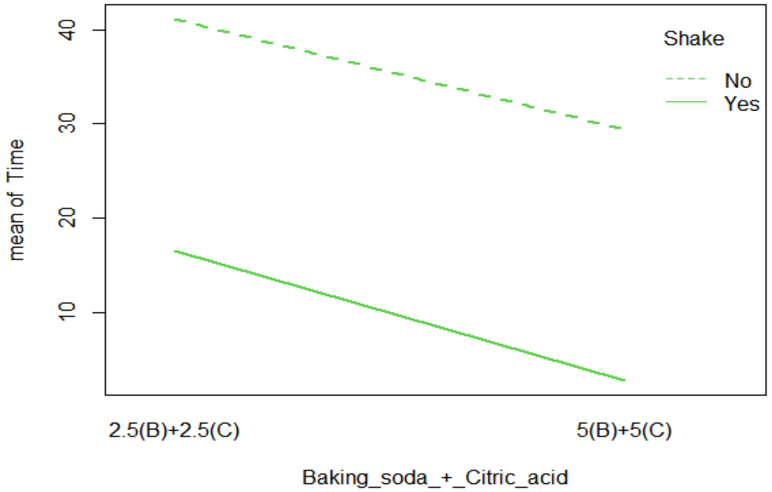


At the level of 7.5 ml water added, shaking the bag seems not that important.

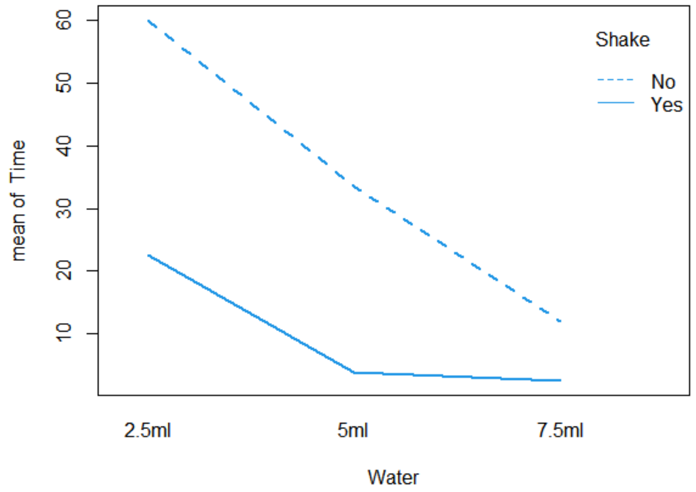
Interaction plot



No significant interaction.



No significant interaction.



Significant interaction. Under the situation of shaking the zipper bag, the explosion time slightly changes as the volume of water added from 5 ml to 7.5ml.

ANOVA Table

$$y_{ijkl} = \mu + \alpha_i + \beta_j + \gamma_k + (\alpha\beta)_{ij} + (\alpha\gamma)_{ik} + (\beta\gamma)_{jk} + (\alpha\beta\gamma)_{ijk} + \varepsilon_{ijkl}$$

$$i = 1,2; \quad j = 1,2,3; \quad k = 1,2; \quad l = 1,2,3$$

$$\varepsilon_{ijkl} \sim^{iid} N(0, \sigma^2)$$

H_0: The factor (or the interaction of factors) affects the explosion time

H_1: Not H_0

```
                                    Df Sum Sq Mean Sq F value   Pr(>F)    
`Baking_soda_+_Citric_acid`          1   1462    1462   4.365 0.047470 *  
Water                                2   7164    3582  10.697 0.000477 ***
Shake                                1   5875    5875  17.545 0.000327 ***
`Baking_soda_+_Citric_acid`:Water    2    183      92   0.274 0.762701    
`Baking_soda_+_Citric_acid`:Shake    1     10      10   0.029 0.866831    
Water:Shake                          2   1265     633   1.889 0.173014    
`Baking_soda_+_Citric_acid`:Water:Shake  2   1480     740   2.210 0.131491    
Residuals                           24   8037     335                     
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Interaction terms aren't significant

ANOVA Table-new model

H_0: The factor affects the explosion time

H_1: Not H_0

```
                            Df Sum Sq Mean Sq F value   Pr(>F)    
`Baking_soda_+_Citric_acid`  1   1462    1462   4.128 0.050821 .  
Water                        2   7164    3582  10.117 0.000415 ***
Shake                        1   5875    5875  16.594 0.000298 ***
Residuals                   31  10976     354                     
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

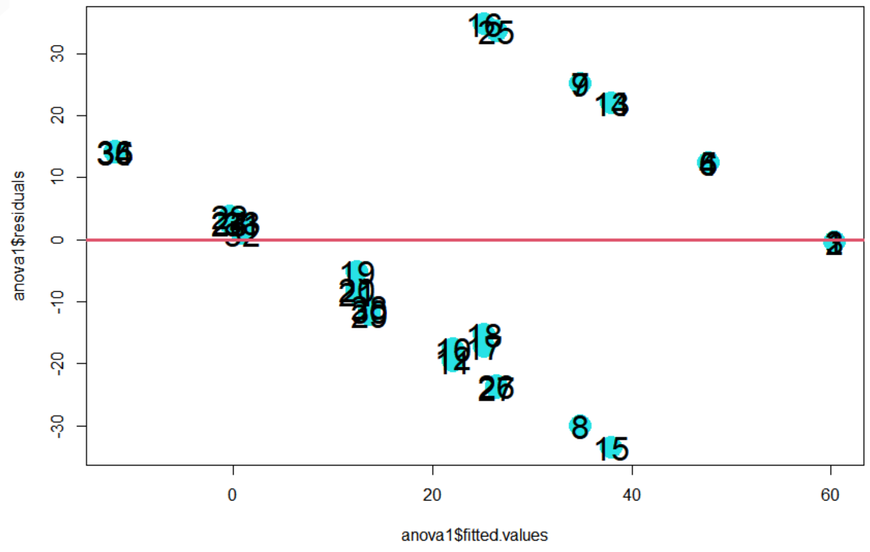
The factor of grams of baking soda and citric acid may not affect the explosion time.
The factor of water and shake may affect the explosion time.

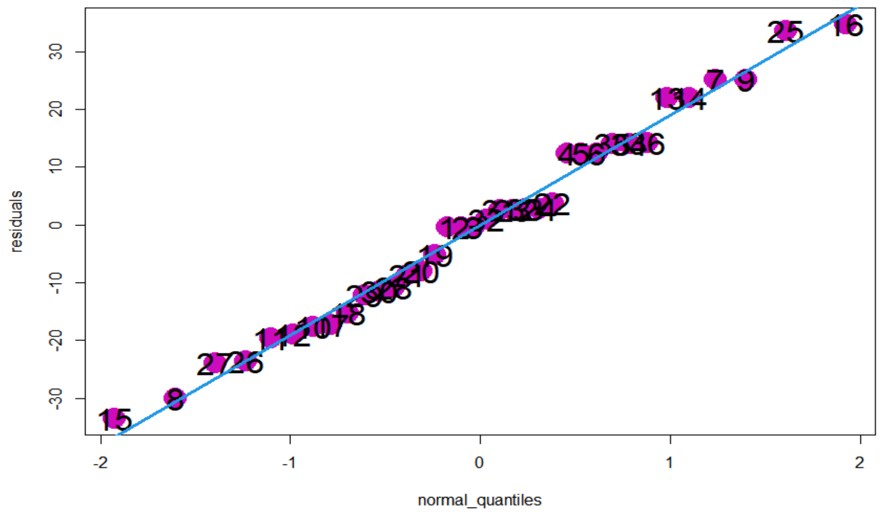
ANOVA Table-new model

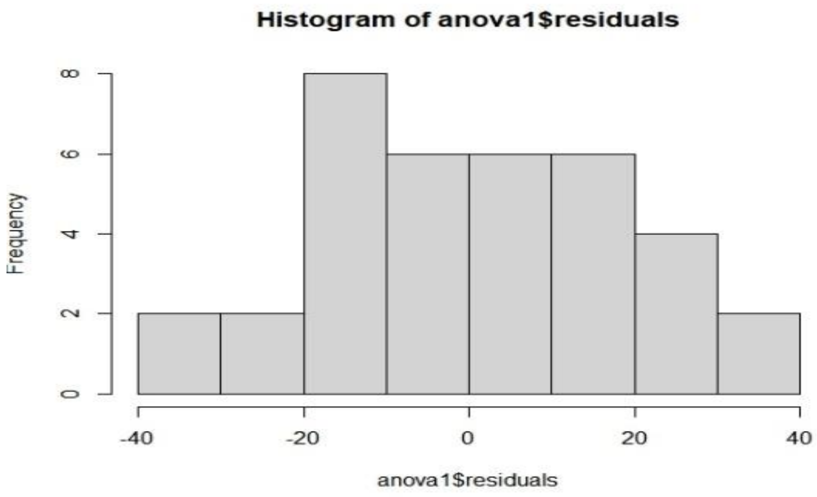
Parameter estimation:

```
Call:
lm(formula = Time ~ `Baking_soda_+_Citric_acid` + Water + Shake)

Residuals:
    Min      1Q  Median      3Q     Max 
-33.552 -12.927   0.268  12.741  34.802 

Coefficients:
                                    Estimate Std. Error t value Pr(>|t|)    
(Intercept)                           60.408      7.013   8.614 9.95e-10 ***
`Baking_soda_+_Citric_acid`5(B)+5(C) -12.744      6.272  -2.032 0.050821 .  
Water5ml                             -22.466      7.682  -2.925 0.006398 ** 
Water7.5ml                           -33.971      7.682  -4.422 0.000112 ***
ShakeYes                             -25.551      6.272  -4.074 0.000298 ***
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 18.82 on 31 degrees of freedom
Multiple R-squared:  0.5692,	Adjusted R-squared:  0.5136 
F-statistic: 10.24 on 4 and 31 DF,  p-value: 2.107e-05
```

Assumption verification







- The residuals vs. fitted values plot shows some pattern. And the residuals do not lie around the 0 line whereas the variances are large.
- In Q-Q plot, the data points closely follow the straight line at a 45% angle upwards. It shows that the residuals are normally distributed.
- 15th observation and 16th observation.

Assumption verification

Homogeneity of variance assumption

H_0: The residual variances are homogeneous

H_1: Not H_0

```
Non-constant Variance Score Test
Variance formula: ~ fitted.values
Chisquare = 1.238056, Df = 1, p = 0.26585
```

Independence assumption

H_0: The residuals have first-order serial correlation

H_1: Not H_0

```
lag Autocorrelation D-W Statistic p-value
  1      -0.1653723      2.312158   0.742
Alternative hypothesis: rho != 0
```

Normality assumption

H_0: The residuals follow normal distribution

H_1: Not H_0

```
        Shapiro-Wilk normality test

data:  anova1$residuals
W = 0.97771, p-value = 0.6678
```

The model with no interaction terms does not violate the assumptions of independence of errors, normality of errors and the homogeneity of error variances. Therefore, the model is considered valid.

Conclusion

- Volume of water added affects the explosion time. The more water added, the quicker the zipper bag explodes.
- Whether to shake the zipper bag affects the explosion time as well. Shaking the zipper bag during the chemical reaction speeds up the time to explode.
- There are no significant interactions between the three experiment factors.

- In addition, the explosion time did not drop much if we add more water or shake the bag. We assume that it is because the domain of time is greater than or equal to 0, the change in time will not be that significant.
- In the future, we may change the size of zipper bag to see if the explosion time would significantly decrease as there is much room for the carbon dioxide gas. Also, there may be some operational errors. What we can improve is repeating more times in each treatment. The result would be more representative.

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- Paper : https://iopscience.iop.org/article/10.1088/2053-1591/ab7e6d/meta

Q&A