TP15443E

CHLORINE RELEASE FROM HYPOCHLORITES

Project Report

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Disclaimer

1. The report was prepared as an account of work conducted by Parole Laboratories Inc., to investigate Chlorine release from hypochlorites. The project T8080-170164, “Chlorine release from hypochlorites,” involved an investigation of reactions of certain products based on sodium hypochlorite with hydrochloric acid and reactions of certain products containing calcium hypochlorite, Trichloro-S- Triazinetrione and Sodium dichloro-s-triazinetrione dihydrate with water.
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Finally, I wish to thank my family and friends for their support and encouragement throughout this project.

Oleg Nepotchatykh, Ph.D.

List of Abbreviations

A – pre-exponential factor in Arrhenius equation

ADC – Analog to digital converter

E_a – Energy of Activation in Arrhenius equation

HPLC – High Performance Liquid Chromatography

ID – Internal Diameter

m/z – ratio of mass to charge of an ion in Mass Spectrometer

MS – Mass Spectrometer

NaDCA – Sodium Dichloro-s-triazinetrione dihydrate

OSHA – Occupational Safety and Health Administration

pH – Potential of Hydrogen

PTFE – Poly Tetra Fluor Ethylene, Teflon ™

RPM (or "rpm") – Revolutions per Minute is a measure of rotation frequency (rotation speed). In the present report's context "rpm" is the rotation speed of the magnetic stirrer bar inside of the reactor

RSD – Relative Standard Deviation

SKC – A corporation, manufacturer of gas sampling bags and other sampling equipment

T – Absolute Temperature

TCA – Trichloro-S-Triazinetrione

UV-Vis – Ultra Violet and Visible (spectral range)

Definitions

Analog to Digital Converter: is an electronic device designed to measure an analog (continuous) signal (such as a signal of a temperature sensor) and to convert the value of the measured signal to a binary code that could be transmitted to a computer.

Destructive Test Method: an analytical method which requires consumption or damage of a sample or part of it for analysis to be made. Examples: HPLC, titration, Mass Spectroscopy;

Initial rate: is the rate of reaction at the so-called time zero (t=0). Refer to Appendix 1 for more information.

LabView: A laboratory automation graphical programming language, developed by National Instruments Co. and widely used for laboratory automation and data acquisition.

Laminar flow: A type of fluid flow in which the fluid flows in parallel layers without turbulent mixing.

Matrix effect: Influence of composition of matrix (media) on the yield of reaction; components of a mixture or impurities could react with a product and lower the reaction product quantity.

Non-destructive Test Method: a test method that not requires sample consumption or its damage. Examples: adsorption spectroscopy, polarimetry, ultrasonic testing, radiography.

Tedlar™: a fluoropolymer, Polyviniliden fluoride.

The t=0: is defined as a moment when reactants completely mixed together at their higher concentration and as a result the reaction rate is at its maximum. Time point of t=0 is located on the time axis somewhere after the end of acid addition. Refer to Appendix 1 for more information.

Thermostat: An automatic laboratory instrument designed to keep temperature of a reactor or other part of an experimental setup at a constant pre-set value.

Thermostated: means that the temperature of a liquid, gas or part of a setup controlled by a thermostat and maintained at a pre-set value.

Viton™: Fluorinated elastomer, copolymer of fluorinated ethylenes.

Virtual instrument: a program in LabView language designed for particular laboratory application and hardware.

Table of Contents

Table of Figures

List of Tables

1. Introduction

Hypochlorites are salts of hypochlorous acid (HClO) and can be formed by a disproportionation reaction between chlorine gas and strong bases as metal hydroxides (Pamphlet 96 Sodium Hypochlorite Manual, 2017). Hypochlorites are generally safe to use but may pose significant health hazards when used inappropriately. The number of accidents involving hypochlorites has been steadily rising in the past decade. Of the 272 incidents involving products containing hypochlorite reported to CANUTEC (Canada, 2017), 75% of these involved solutions containing less than 7% active chlorine (UN 1791). Given this fact, the oxidation power of such weak solutions is questionable. The remaining 25% of accidents involved solid calcium hypochlorite, where oxidative reactions become more probable.

Hypochlorites such as sodium hypochlorite NaOCl, calcium hypochlorite $Ca(OCl)_2$, Trichloro-S-Triazinetrione (Trichloroisocyanuric acid or TCA) $C_3Cl_3N_3O_3$ and Sodium dichloro-s-triazinetrione dihydrate (Sodium dichloroisocyanurate or NaDCA) $NaC_3H_4Cl_2N_3O_5$ are widely used as effective disinfecting and cleaning agents (William A. Rutala). Sodium hypochlorite is unstable in pure form, and it is sold as an aqueous solution (household bleach). These solutions contain 3 to 15% of NaOCl with 0.25 to 0.35% free alkali such as NaOH and 0.5 to 1.5% NaCl. Calcium hypochlorite, Trichloroisocyanuric acid, and Sodium dichloroisocyanurate are stable in solid form and therefore sold as a powder, granules or pellets used for swimming pool water treatment.

The real danger posed by hypochlorites is mainly due to their decomposition, resulting in the release of chlorine gas, the main concern in poorly ventilated areas. Chlorine gas is corrosive and depending on the concentration released, route of exposure and exposure time can be highly toxic.

Severe acute effects of chlorine exposure in humans have been well documented since World War I when chlorine gas was used as a chemical warfare agent (Gilchrist, 1933). Other severe exposures have resulted from the accidental rupture of chlorine tanks. These exposures have caused death, lung congestion, pulmonary edema, pneumonia, pleurisy, and bronchitis. The lowest lethal concentration reported is 430 ppm for 30 minutes. Exposure to 15 ppm causes throat irritation, exposures to 50 ppm are dangerous, and exposures to 1,000 ppm can be fatal, even if the exposure is brief (Bjarnason, 2004).

The most common causes of hypochlorite product decomposition include:

a. Wetting

This is generally the case with solid hypochlorite products, such as calcium hypochlorite, trichloroisocyanuric acid and sodium dichloroisocyanurate. Calcium hypochlorite concentration found in powdered or tablet form is generally between 60-99%. Because of its high concentration, calcium hypochlorite is intended to be mixed with large volumes of water. If accidentally mixed with a small volume of water, a vigorous exothermic reaction may occur, resulting in a sudden increase in temperature and release of toxic chlorine gas (eq. 1).

$$Ca(OCl)_2 + H_2O \rightarrow Cl_2\uparrow + Ca(OH)_2 + \tfrac{1}{2}O_2 \qquad (1)$$

It is expected, that both trichloroisocyanuric acid and sodium dichloroisocyanurate in solid powder form would also release chlorine gas when mixed with a small volume of water.

b. Combining with incompatible material

The principal situation leading to dangerous hypochlorite decomposition arises when its salts are mixed with cleaning products containing acids, such as hydrochloric acid. Many household cleaners contain up to 10% HCl to improve their cleaning efficiency. Upon mixing, the liberation of toxic chlorine gas occurs, which may result in acute burns and serious health effects depending on the speed and amount of toxic chlorine gas that is released (eq. 2):

$$NaOCl + 2HCl \leftrightarrow NaCl + H_2O + Cl_2\uparrow \qquad (2)$$

This equilibrium is pH-dependent (Le Châtelier’s principle), where high pH drives the reaction to the left promoting NaOCl formation, whereas a low pH drives the reaction to the right, promoting the release of chlorine gas, Cl_2.

2. Objectives

The main objective of this study was to determine the amount of chlorine gas release from hypochlorites in commonly used forms such as solutions, solids or powders when they are mixed with hydrochloric acid (HCl) or water. The results of this study will support recommendations delivered by Canadian Transport Emergency Centre (CANUTEC) to the members of the public during incidents involving these chemicals. Furthermore, these results will help the public to educate themselves on proper use of common household cleaning agents and pool chemicals to reduce the likelihood of accidents and injuries resulting from the use of products containing hypochlorites.

The work was carried out by Parole Laboratories Inc. and it consisted of the following tasks:

2.1. Task 1: Calibration Curve Generation

It is important to know the minimal and maximal ratios of product/acid or product/water that can result in chlorine gas release. This is important because a hypochlorite containing product may be accidently mixed with different amounts of hydrochloric acid or water and as a result, various volumes of chlorine could be released. For example, a small portion of hydrochloric acid added to a sodium hypochlorite product will react completely with NaOH (which is always present in sodium hypochlorite products) and not result in chlorine release. Also, it is important to estimate the amount of hydrochloric acid that will result in a complete decomposition of sodium hypochlorite, so adding more hydrochloric acid will not produce more chlorine gas. One can expect a strong dependence of min/max hydrochloric acid amounts on the sodium hypochlorite concentration.

The objective of Task 1 was to quantify the amount of chlorine gas that is released from sodium hypochlorite and calcium hypochlorite of laboratory grades depending on the amount of hydrochloric acid or water added.

On the first part of Task 1, distinct calibration curves will be generated to quantify the chlorine gas released during the titration of various concentrations of sodium hypochlorite (ranging from 0 — 15% of NaClO) with repeated additions of 10% hydrochloric acid solution at three initial temperatures (15, 22, and 30°C).

On the second part of Task 1, distinct calibration curves will be generated to quantify the chlorine gas released during the titration of various concentrations of calcium hypochlorite (ranging from 60 to 99% of calcium hypochlorite) with water at three initial temperatures (15, 22, and 30°C).

In both parts of Task 1, laboratory grade chemicals were used to avoid matrix effects expected for household products (see Task 2 objectives).

2.2. Task 2: Assessing Chlorine Release Efficiency

Under Task 2, the efficiency of chlorine gas release from common household products was investigated. The hypothesis was that components present in the hypochlorite products (e.g. stabilizers and additives) may interfere with the rate and yield of the chlorine gas release, the phenomenon which is referred to as a matrix effect. For instance, HCl could react mainly with NaOH, present as a stabilizer in liquid hypochlorite products, without causing release of chlorine. Reactions of elemental chlorine with organic ingredients or impurities can also result in significant matrix effect. In addition, some matrix effect could be caused by solubility of chlorine in the reaction mixture. Some chlorine can remain dissolved in the liquid phase if the reaction happens in a closed system due to the equilibrium with chlorine in the gas phase. In the event there is moving air over the reaction mixture, dissolved chlorine will evaporate and, accordingly, the total amount of chlorine released into the air is expected to be higher.

The objective of the Task 2 was to determine chlorine release efficiency from 6 hypochlorite-based household products. To do so, each product was analyzed iodometrically to determine actual concentration of hypochlorite (active chlorine). The theoretical amount of chlorine release was calculated based on the actual concentration of active chlorine in each of the products. Three liquid products were reacted with hydrochloric acid and 3 solid products were reacted with water to determine actual chlorine release. The amount of chlorine gas released from each product was compared to the theoretical amount expected for each product based on the reaction stoichiometry. All experiments were conducted at 3 different temperatures to assess the influence of the temperature. The matrix effect caused by chlorine solubility in the reaction mixture was estimated as a difference in results obtained using closed and vented setups as vented setup simulates “open container” conditions with moving fresh air over the reaction mixture.

2.3. Task 3: Assessing the Speed of the Reaction

It is important to assess the rate of reactions resulting in the release of chlorine gas because a hypochlorite product can accidentally be mixed with hydrochloric acid or water and can release chlorine with different speed (rate). If chlorine is released at a high rate, this can result in a very high local chlorine gas concentration (a cloud), which may be potentially fatal if inhaled. In contrast, a slow chlorine release may be not dangerous, or may potentially pose some risk if released over a long period of time in a poorly ventilated room.

The objective of the Task 3 was to assess the speed of the reaction of chlorine release. Under Task 3, kinetic parameters of reactions of 3 liquid products with HCl and 3 solid products with water at 3 temperatures (15, 22, and 30°C) were measured. As a result, Arrhenius parameters that allow prediction of reaction rate at any temperature for each product were estimated.

2.4. Task 4: Assessing the Effect of Mixing on the Rate of Reaction

It is necessary to determine the effects of different mixing speeds on the rate of the reactions resulting in chlorine gas release. A hypochlorite product could be accidently mixed with an acid or water slowly and the release of chlorine gas could be slow, or be added quickly and intensely mixed or shaken, which could result in fast chlorine gas release. Therefore, one can expect that the chlorine gas release rate will depend on mixing speed and pose a different degree of a danger.

The objective of the Task 4 was to assess the effect of mixing speeds on the rate of reaction. Under the Task 4 kinetic parameters of reactions of 3 liquid products with HCl and 3 solid products with water at 3 temperatures (15, 22, and 30°C) and at 4 different mixing speeds (0, 50, 100 and 300 rpm) were measured.

3. Materials and Methods

3.1. Materials

Table 1. Materials and reagents used in the project

Name	Source
Sodium hypochlorite solution reagent grade 15%,	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Hydrochloric acid ACS reagent, 37%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Sodium carbonate ACS reagent, anhydrous, ≥99.5%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Sodium thiosulphate 98%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Sulphuric acid ACS reagent, 95.0-98.0%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Potassium iodate ACS reagent, 99.5%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Potassium iodide ACS reagent, ≥99.0%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Starch, soluble	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Chlorine, liquefied gas ≥99.5%	Sigma-Aldrich Canada Co., Oakville, Ontario, Canada
Water	produced on-site using Milli-Q ® plus ultra-pure water system, France
Javel-12	Sany Inc., Joliette (Qc) Canada
Liquid Plumr by The Clorox Company of Canada	Wal-Mart
Ultra San	Ecolab, Québec, QC, Canada
Super Shock by HTH	Club Piscine, Kirkland, QC Canada
Stabilized chlorinating granules by HTH	Club Piscine, Kirkland, QC Canada
Stabilized chlorinating pucks by HTH	Club Piscine, Kirkland, QC Canada

3.2. Methods

3.2.1. Setup configuration: Theoretical background

The kinetic experiments performed for the Tasks 3 and 4 as well as for the titration experiments of Task 1 required that the released chlorine gas remains inside of a setup and its concentration had to be measured periodically or continuously. This allowed accurate measurement of reaction rates. The UV-Vis spectrophotometry was chosen as the best analytical method for accurate chlorine concentration measurement within this project. Please refer to the Appendix 3 for detailed information.

During a hypochlorite reaction, a large volume of chlorine gas, 1 to 3 liters at normal conditions, is expected to be released from a hypochlorite sample of chosen size (about 0.1 mol), according to the gas law (eq. 3)

$$PV=nRT \tag{3}$$

The released volume of chlorine gas will either increase the pressure (P) or the volume (V). In equation (3) n is the molar concentration, R is the gas constant and T is absolute temperature. In order to contain and measure the released chlorine, the setup must be designed in such a way to either keep a constant volume (pressure will increase) or constant pressure (volume will increase). In a hermetically closed all-glass reactor in which the volume is constant, the release of chlorine gas will create a significant pressure increase, according to the gas law. This increase in pressure inside the setup is not desirable since this will most probably result in a catastrophic situation such as reactor rupture, pop-up, or major chlorine leak into the laboratory.

Another reason to avoid pressure build-up in the setup is that it lowers the integrity of the applicability of the experiments. In a situation of a household accident, the reaction will most probably occur in an open area or vessel at atmospheric pressure. Therefore, the experiment conducted at an increased pressure condition will report lower chlorine release than it at household accident conditions (at the atmospheric pressure) because the solubility of chlorine in water is higher at a higher pressure. The proper setup for this study must be designed in the way to keep the constant pressure inside of it. The setup must be able to change volume without considerable change of pressure and be hermetic at the same time, so all gases remain inside of the setup.

The experiments under the Task 2 were carried out using the “closed” setup described above. However, in the closed setup, some chlorine remains dissolved in the liquid phase due to the equilibrium with the gas phase chlorine. As mentioned above in case of an accident when the air is moving across the reaction mixture the dissolved chlorine evaporates into the air. To simulate such a condition a second, so-called “vented” setup was used. In the vented setup a constant flow of clean air was passed through the reactor and chlorine was detected in the exiting gas mixture. The result of measurement is pretty similar to a chromatogram in nature; the quantity of released chlorine was calculated as an area between the “chlorine signal” curve and baseline. Unlike in the “closed” setup the “chlorine signal” curve that was made using the “vented setup” could only be expressed as optical absorption unit and not in chlorine concentration units. This curve produced by the vented setup cannot be used for kinetic experiments because the whole curve represents one single measurement of a total chlorine amount that has been released. In contrast, the signal curve obtained using closed setup represents multiple chlorine concentration measurements at multiple time points and can be recalculated using calibration parameters from optical adsorption units to concentration units and it is therefore perfect for kinetic measurements. This is the reason why vented setup can only be used for Task 2.

3.2.2. Closed setup construction and operation

As mentioned above, in the “closed setup”, the pressure remained constant and the volume changed when chlorine release occurred. As a volume expansion device, a 5 liters gas sampling bag made of Tedlar by SKC part # 232-05 was used. The Tedlar film is a fluoropolymer and it is resistant to chlorine and there is virtually no diffusion of chlorine or air through this film. Together with the excellent flexibility, this made it a good volume expansion device. During the reaction, the released chlorine gas was mixed with the air inside the setup and excessive volume of gas mixture entered the gas bag. As a result, the volume inside the setup increased, and the pressure remained constant. The Tedlar bag did not create any excessive pressure and served both as an expanding container for released chlorine gas and as an excellent pressure equilibrating device. The setup was hermetic during the experiment, all released chlorine gas remained inside. The schematic diagram of the closed setup is presented below:

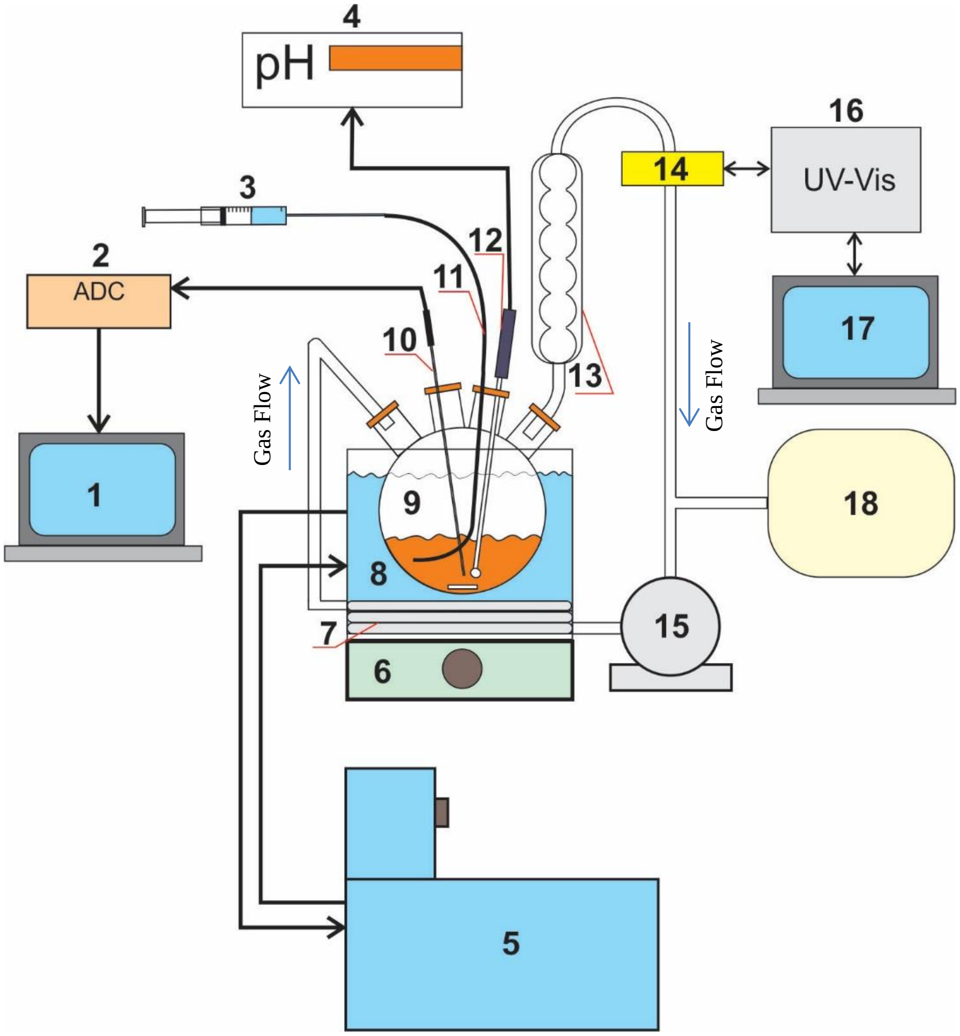


Fig. 1 Closed setup for study of chlorine release from hypochlorites

Table 2. Numbers and names of setup parts in Fig. 3

Part #	Part name
1	Computer for temperature sensors and thermostat
2	16 bit analog-to-digital signal converter;
3	Metering syringe for acid or water injection
4	Digital pH-meter
5	Refrigerated thermostat with in- and out- pumps
6	Digital magnetic stirrer
7	Coil of PTFE tubing used as gas heat exchanger
8	Thermostated water bath
9	Reactor
10	Temperature sensor
11	PTFE capillary for injection of acid or water into the reactor
12	pH electrode

13	Reflux condenser
14	Spectrophotometric gas flow cell
15	Gas pump
16	UV-Vis spectrophotometric detector
17	Computer for spectrophotometric detector
18	Tedlar expansion gas bag

The setup presented in Fig.1 was composed of a glass reactor (9), placed in a thermostatic water bath (8), the bath (8) was connected to a refrigerated thermostatic circulator (5) made by Neslab. The bath (8) was placed on top of a digital magnetic stirrer made by PO-Labs (6); the digital magnetic stirrer allowed precise stirring of the reaction mixture in the reactor (9) by means of a magnetic stirring bar placed in the reactor (9). Accurate and fast measurement of the quantity of released chlorine required intense mixing of the gas phase inside of the reactor (9). The mixing of the gas phase was performed by gas pump (15) model UN79MNI made by KNF Gmbh. The pump was custom designed in a way that all of its parts (valves, membrane, head) that can come in contact with the aggressive pumping gas made of PTFE.

The circulation of the gas phase in the setup was as follows: Gases from the reactor (9) passed through reflux condenser (13) (to separate excess moisture from the gas), then the gas mixture was directed into the spectrophotometric cell (14) connected to spectrophotometer (16) (Beckman systems 166) and computer running Beckman 32-Karat HPLC software. Next, the gas mixture was directed to the inlet of the pump (15). The outlet of the pump (15) was connected to the PTFE tubing coil placed inside of the water bath to equilibrate temperature of the gas mixture with the reactor's temperature. The outlet of the PTFE tubing coil was connected back to the reactor, and so closing the gas circulation loop. The excessive volume of gas mixture released as a result of the hypochlorite reaction entered the gas bag (18). The reactor (9) was equipped with the temperature sensor (Omega p/n 44005) protected with PTFE and connected to the instrumental amplifier made by PO-Labs, then to a 16-bit ADC (Ontrak ADU-100) (2) and a second computer (1) running LabView virtual instrument, programmed by PO-Labs. The instrumentation allowed reactions to be carried out at pre-determined temperatures (15, 22, and 30 °C). It also allowed to continuously record any temperature changes inside the reaction mixture during the reaction. The temperature registration system has an accuracy of 0.001 °C and the thermostatic system kept the reactor at the pre-set temperature to within ±0.2°C deviation. The reactor was also equipped with a combination of pH electrode (12) and pH-meter (4) to record changes of pH for Task 1. All parts of the setup that could contact liquid or gas reaction phase were made either of glass, PTFE, Viton or fused silica; those materials are resistant, inert and impermeable to wet and dry chlorine as well as other gases.

Experiments were run as follows: All electronic systems were switched on and equilibrated to the required parameters; the thermostat (5) was stabilized the required temperature. An aliquot of liquid or solid hypochlorite product was then placed into the reactor (9). The 10% solution of hydrochloric acid or water also was brought to a required temperature using the thermostat prior to injection into the reactor, so the addition of one of them into the reactor did not change the initial temperature of the reaction mixture. As soon as the temperature of a product inside of the reactor (9) reached the required value, the reactor was closed hermetically and the acquisition of data was initiated (the spectrophotometer and the temperature logger). At that time, the “zero” baseline was recorded for approximately one minute and then the required amount of hydrochloric acid or water was injected through the capillary (11), this initiated a reaction inside the reactor. During the course of the reaction, it was possible to observe the concentration of chlorine gas and reaction temperature on the computer screens (1) and (17) in the real time (see Fig.2). At the end of the experiment, chlorine gas was evacuated from inside of the setup by means of the pump (15) into the chlorine scrubber and deactivated. Under normal operational conditions the setup did not produce any contamination of the atmosphere.

The photographs of the setup are presented on the following pictures.

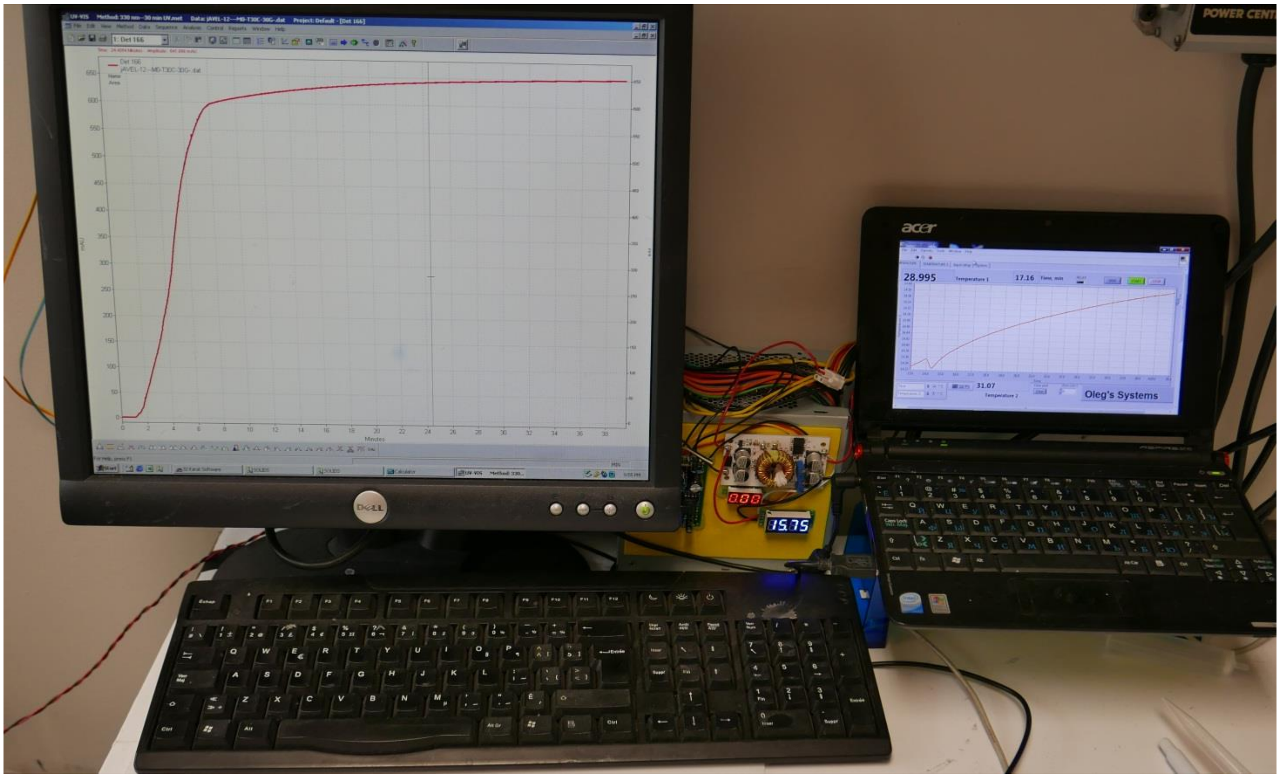


Fig. 2 Closed setup for study of chlorine release from hypochlorites

Computers: for spectrophotometer (left) and for temperature (right), ADC and instrumental amplifier in the middle.

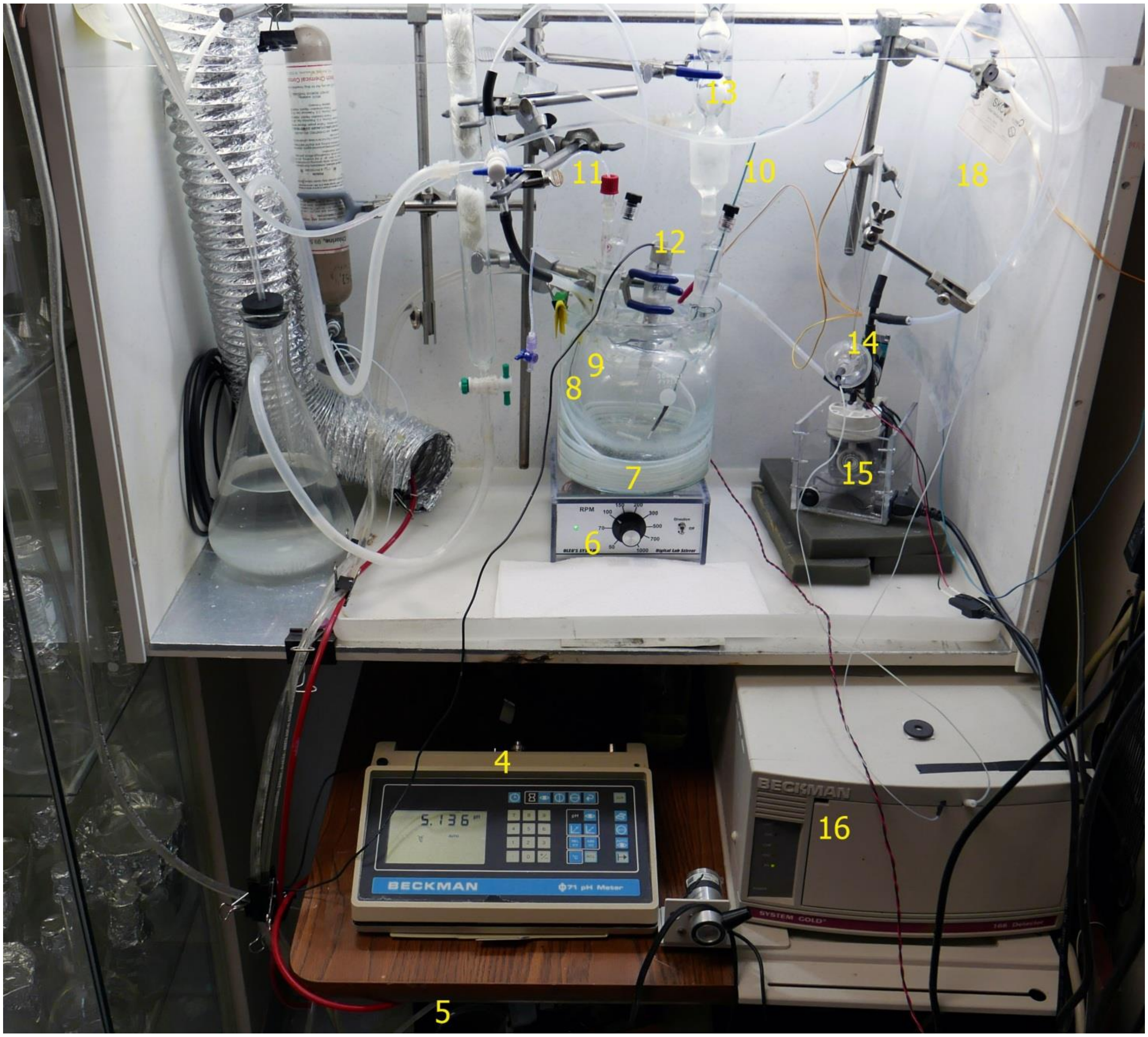


Fig. 3 Closed setup for the study of chlorine release from hypochlorites

Table 3. Numbers and names of setup parts in Fig. 3

Part #	Part name
4	Digital pH-meter
5	Refrigerated thermostat with in- and out- pumps
6	Digital magnetic stirrer
7	Coil of PTFE tubing used as gas heat exchanger
8	Thermostated water bath
9	Reactor
10	Temperature sensor
11	PTFE capillary for injection of acid or water into the reactor
12	pH electrode
13	Reflux condenser
14	Spectrophotometric gas flow cell
15	Gas pump
16	UV-Vis spectrophotometric detector
18	Tedlar expansion gas bag

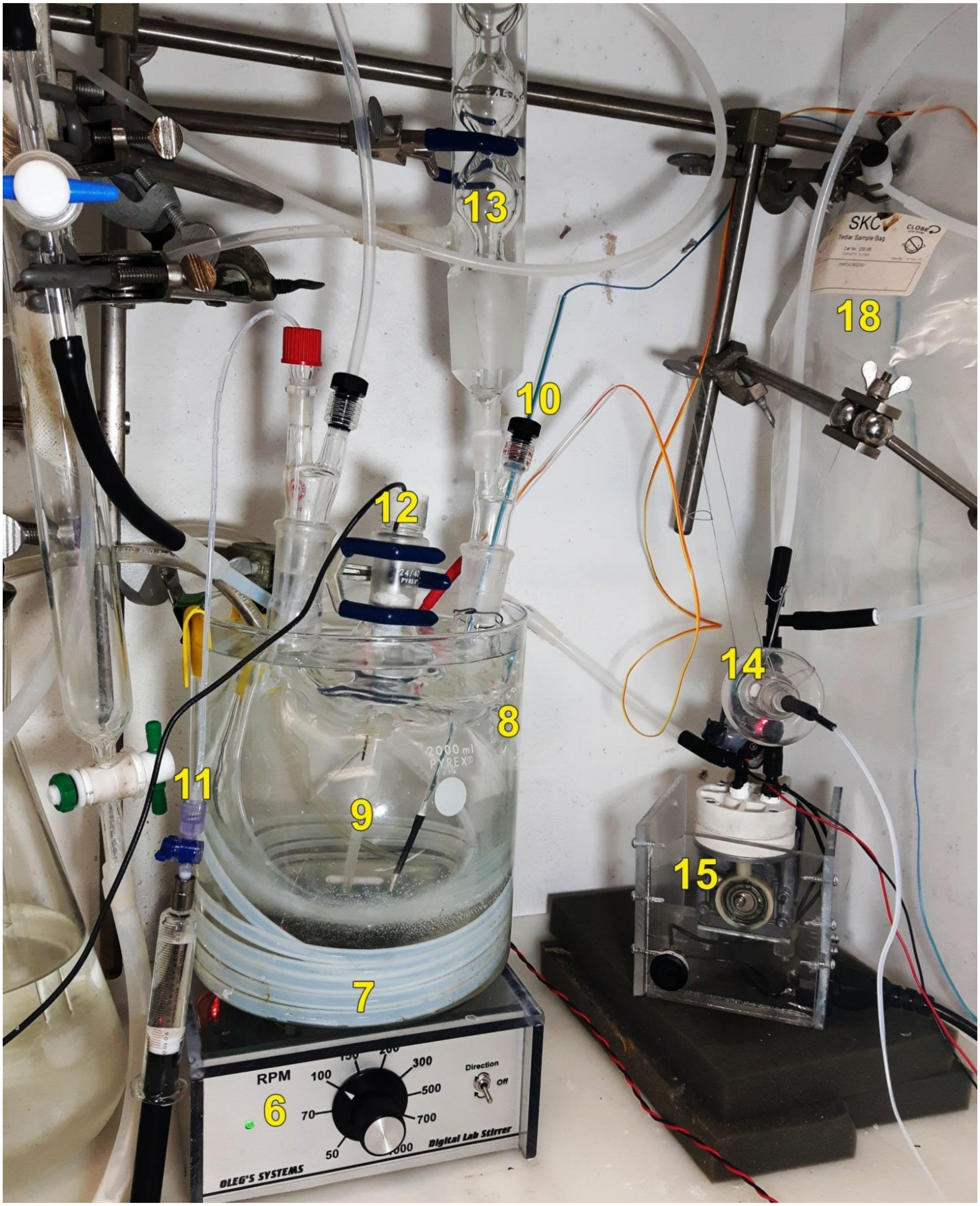


Fig. 4 Close-up view of the setup

The numeration is the same as on the previous picture.

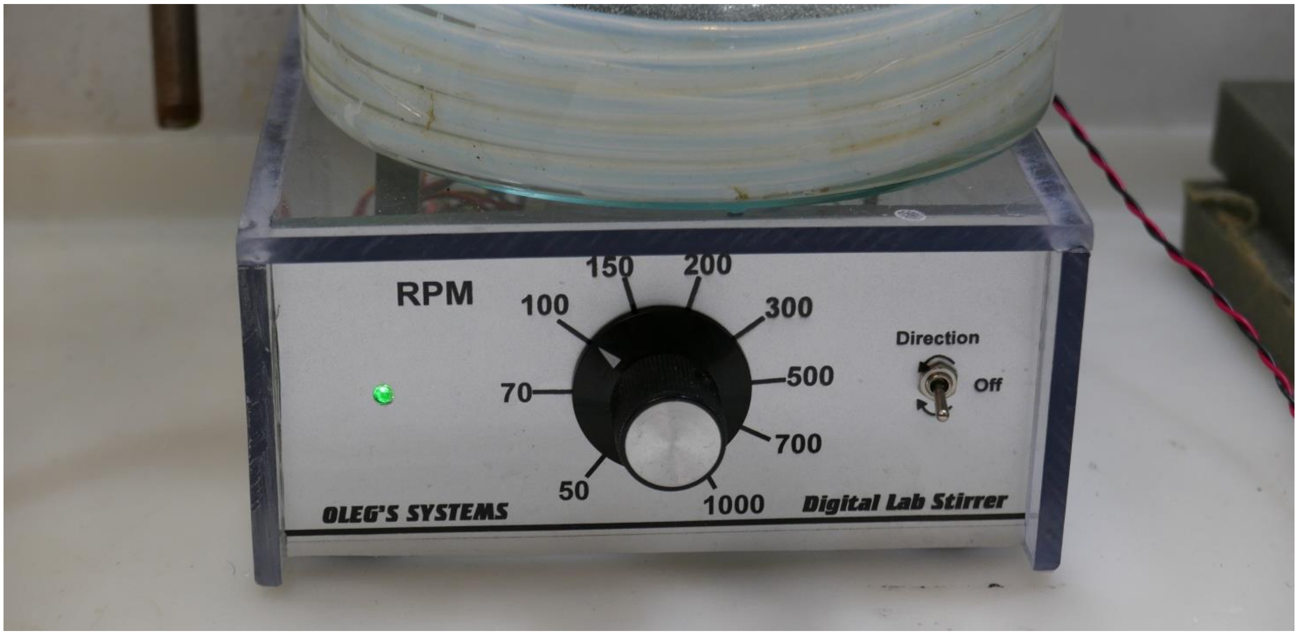


Fig. 5 Picture of digital magnetic stirrer

The experiments in the present study required stirring of the reaction mixture at the precisely fixed mixing speeds: 0, 50, 100 and 300 rpm. Most of commercially available lab stirrers are unable to rotate at precise controllable speed. For this project, was used in-house built lab stirrer based on a stepper motor controlled by quartz-stabilized digital electronics that provided precise pre-defined mixing speeds.

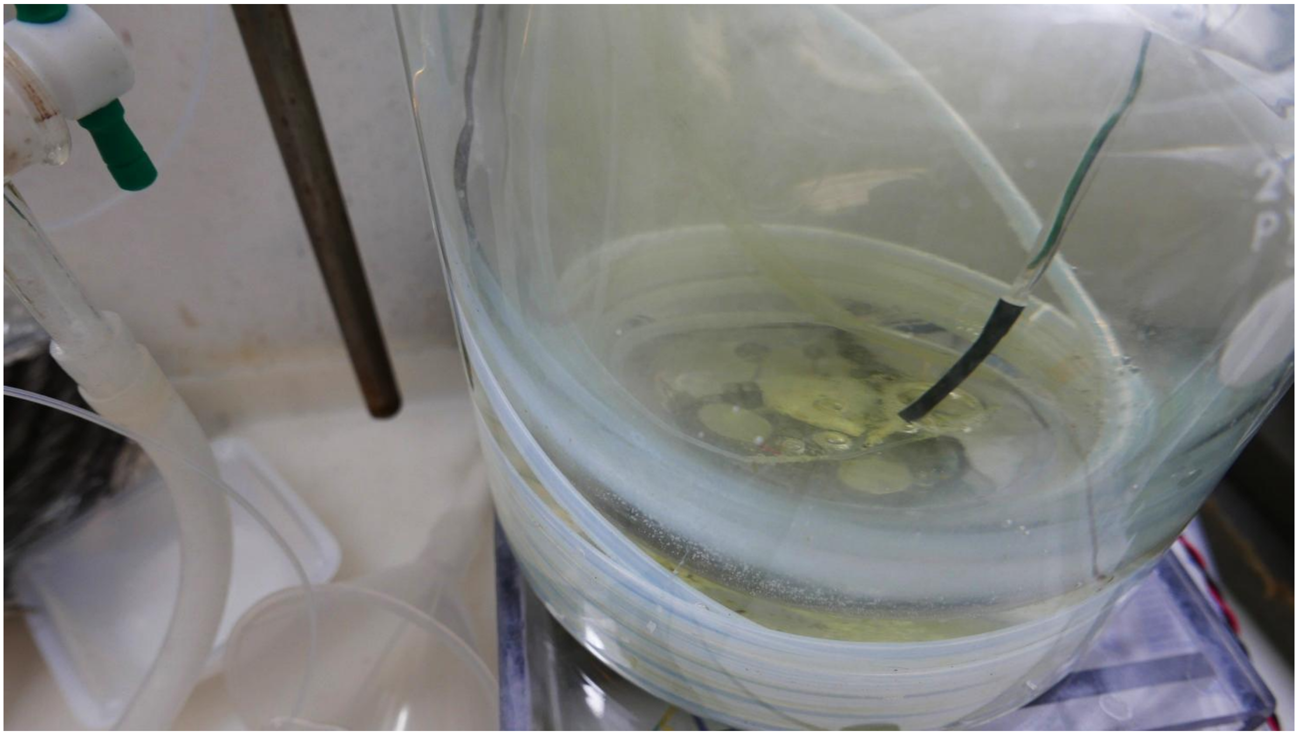


Fig. 6 Picture of the reactor during the experiment

Large bubbles of chlorine are clearly seen on the surface of liquid reaction mixture. Inside of the reactor one can see the PTFE capillary (on the bottom left) and temperature sensor, inserted from the right side of the reactor.

3.2.3. Closed setup calibration and validation

Several important analytical validation parameters of the enclosed setup, such as sensitivity, linearity, repeatability, response rate and range of concentration, have been measured.

The following plot demonstrates the response rate, it is very important for kinetic experiments:

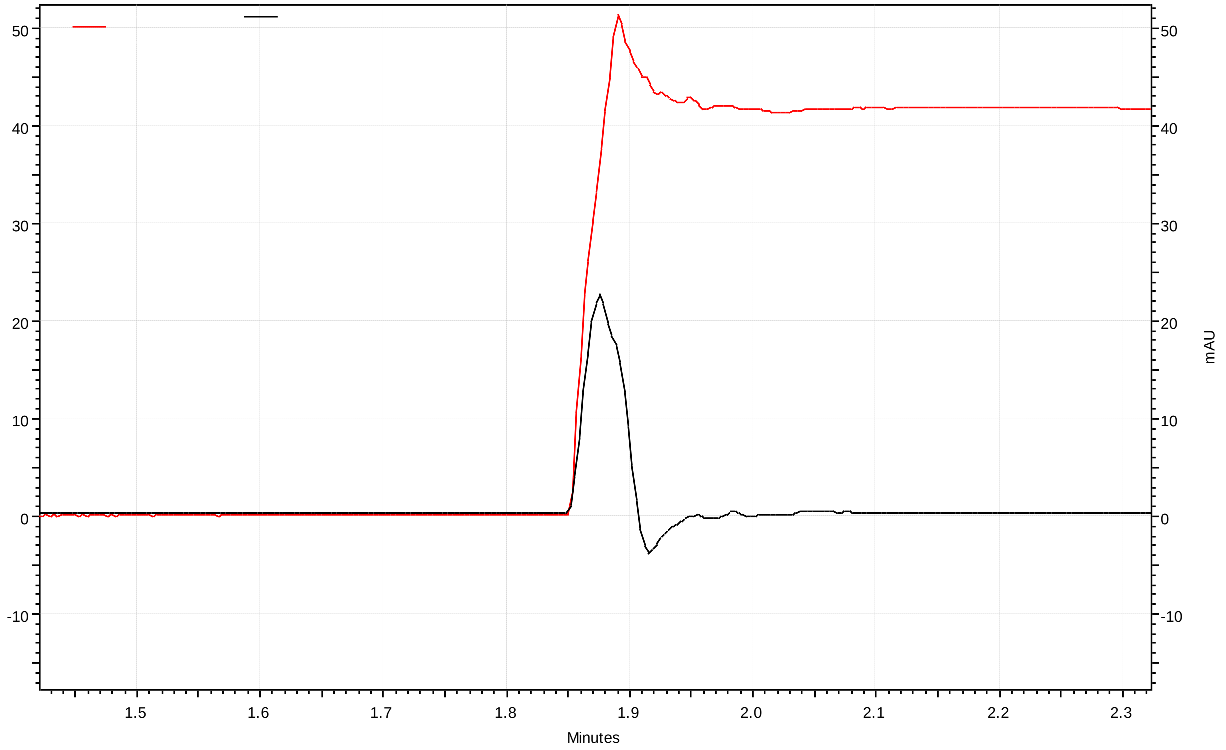


Fig. 7 Detector performance and response time test.

The red trace represents chlorine absorption at 330 nm; the black trace is the 1-st derivative of it, which is the rate of chlorine absorption change.

In this experiment, 50 mL of pure chlorine was injected into the setup and the detector response was recorded. Time of injection was 3 sec, started exactly at 1.85 min. The analytical response was immediate, the time to reach the maximum absorbance was 3 sec (the same amount of time as the chlorine injection time) and complete equilibration required another 1.2 seconds. During this time the pump mixed all of the gas in the setup completely. Equilibration is the small negative part of the black trace. The response rate of the setup to a chlorine injection was difficult to measure because it was a fraction of a second; the equilibration time was 1.2 seconds, which is fast enough for this type of kinetic experiments (Vallance, 2017).

The response of the detector to multiple injections of pure chlorine is demonstrated on the plot below. One can see that each injection produced a fast rise in analytical signal and then the signal remained constant (horizontal) between injections at the same level. On this plot, the red trace is the chlorine absorption and black trace is its 1-st derivative.

This experiment proved that injected chlorine remained inside the setup without changes in concentration, there was no leak and the setup was inert to chlorine:

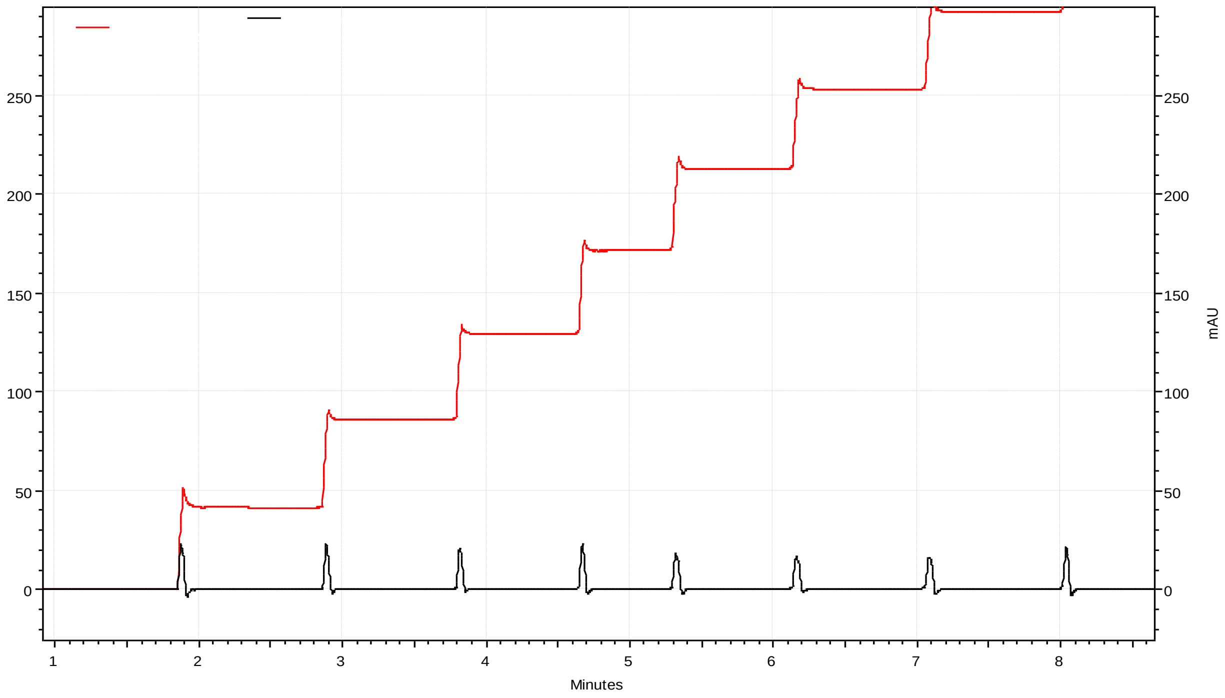


Fig. 8 Response of detector to multiple injections of pure chlorine.

The spectrophotometric detector in the closed setup generated an optical adsorption signal in mAu units, and to convert this signal to chlorine concentration units (such as mol/L) the setup was calibrated using additions of pure chlorine of precisely known quantity. Knowing the quantity of chlorine is essential since it dictates the concentration in a known volume as given by:

$$C = m/v \quad (4)$$

Then the calibration plot was made, which represents the relationship between mAu units and mol/L units:

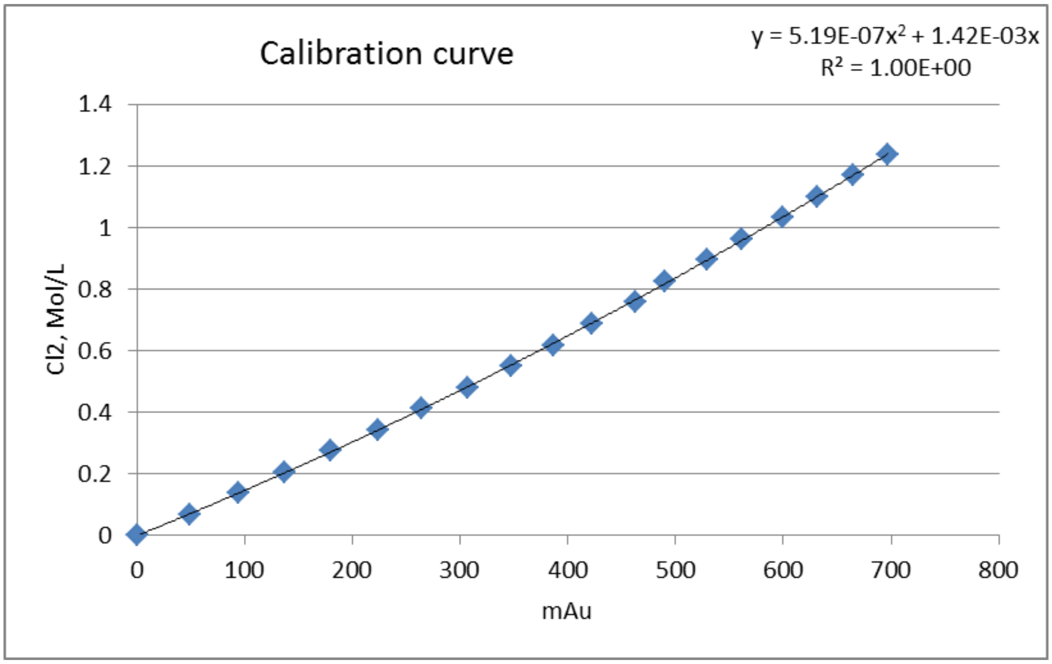


Fig. 9 Calibration plot of the closed setup

3.2.4. Method validation parameters for closed setup:

- Range of quantification was determined as 5 orders of magnitude, from 3.22E-07 to 4.13E-02 Mol/L or 7.8 ppm (part per million, vol/vol) to 1,000,000 ppm chlorine, or the same 0.078% to 100% vol/vol of chlorine;
- The Limit of Quantification was determined as 3.19E-07 Mol/L.
- Limit of detection was determined as 9.6E-08 Mol/L
- Repeatability was determined as RSD = 0.2%;
- Intermediate precision was determined as RSD = 0.51%
- Calibration curve fit was quadratic: y = 5.19E-07x2 + 1.42E-03x; the same as: $[Cl_2]$(Mol/L) = 5.19E-07$(mAu)^2$ + 1.42E-03(mAu)
- Method linearity was determined as $R^2 = 0.9999$
- Stirring speed stability was determined as RSD = 0.002%

It is important to note, that all experiments performed with both vented and closed setups, without exception, included “Zero” readings. The “Zero” reading is located at the beginning of each chlorine signal curve and also at the beginning of each temperature curve. The “Zero” reading has minimum 30-seconds length, typically 1-minute.
After the “Zero” reading period, the HCl or water aliquot was injected into the reactor to initiate the reaction. The “Zero” reading was required for several reasons: to establish a baseline, for accurate concentration calculation, to measure signal to noise ratio in each experiment and to use it as a zero quality control sample.

3.2.5. Vented setup construction and operation

As mentioned above the “vented” setup included a reactor that is vented. This means that clean air flow passed through the reactor at a constant speed at atmospheric pressure and chlorine was detected in the gas mixture (air and chlorine) that exited the reactor. The pump drove the gas mixture at a constant rate and due to the small gas flow and large ID of the reactor inlet, no pressure drop was observed in the reactor. The vented setup schematic diagram is presented below:

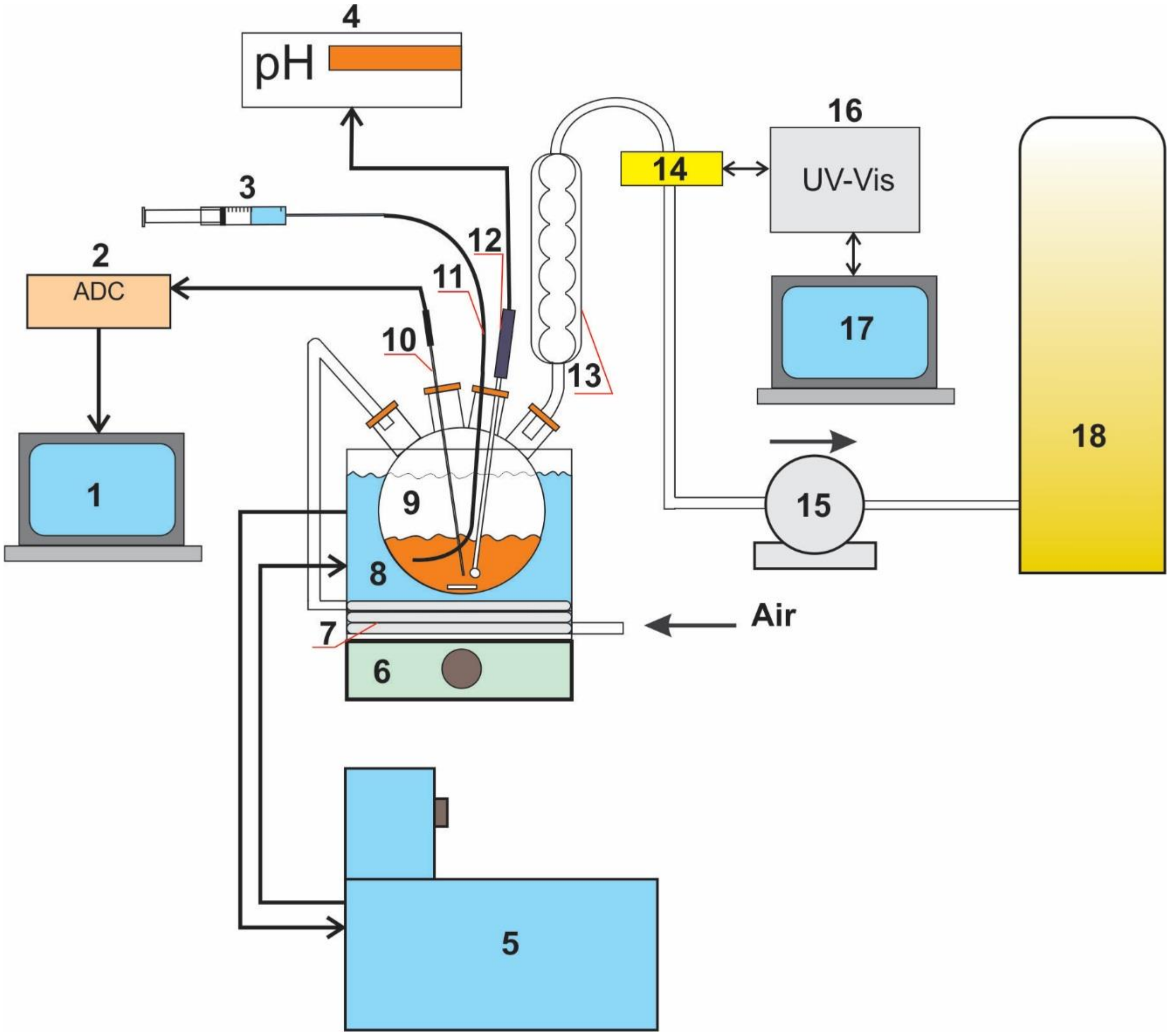


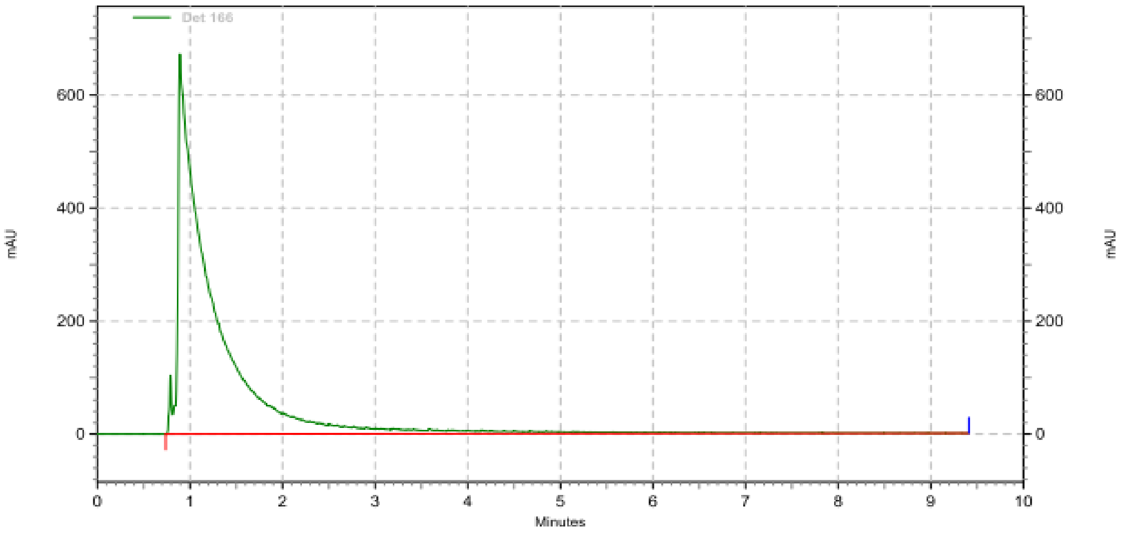
Fig. 10 Vented setup for study of chlorine release from hypochlorites.

Table 4. Setup part numbers and names for the Fig. 10

Part #	Part name
1	Computer for temperature sensors and thermostat
2	16 bit analog-to-digital signal converter;
3	Metering syringe for acid or water injection
4	Digital pH-meter
5	Refrigerated thermostat with in- and out- pumps
6	Digital magnetic stirrer
7	Coil of PTFE tubing used as gas heat exchanger
8	Thermostated water bath
9	Reactor
10	Temperature sensor
11	PTFE capillary for injection of acid or water into the reactor
12	pH electrode
13	Reflux condenser
14	Spectrophotometric gas flow cell
15	Gas pump
16	UV-Vis spectrophotometric detector
17	Computer for spectrophotometric detector
18	Tedlar expansion gas bag

Most of the components included in the vented setup are the same as in the closed setup, the only difference is that in the vented setup, the Tedlar gas bag was not included and a chlorine neutralization scrubber was added (compare Fig.10 and Fig. 1). However, connections of gas lines were different which made the vented setup fundamentally different from the closed setup. The vented setup functioned as follows: Clean air entered the PTFE tubing coil (7) kept at a pre-set temperature where the air assumed the same temperature as the reactor (9), then the air entered reactor (9). Maintaining the preset temperature of the incoming air is required to keep reactor temperature controlled because ambient air may have a different temperature than inside the reactor. Chlorine released during a hypochlorite reaction is carried out of the reactor (9) with the flow of air. The air-chlorine mixture was then passed through the reflux condenser (13) where an excess of moisture was separated and then analyzed by spectrophotometric cell (14), connected to UV-Vis spectrophotometer (16). After the spectrophotometric cell (14), the mixture of gases was forced by the pump (15) into chlorine scrubber (18), where chlorine was deactivated, and the remaining clean air was released into the atmosphere. The scrubber was filled with soda lime pellets and had a sodium thiosulphate indicator layer. The photographic pictures of vented setup are not presented because they are very similar to the closed setup.

The vented setup allowed to measure total chlorine release in conditions similar to household accidents, where moving air facilitates evaporation of dissolved chlorine from the reaction mixture. The vented setup is not suitable for kinetic experiments, because it generates only one concentration result by experiment. Although the chlorine signal can be registered as a continuous curve, this curve represents a single concentration result which was calculated based on the area between baseline and the chlorine signal curve. This calculation was done using the standard chromatographic software, Beckman 32-Karat HPLC. The chlorine signal registered with the vented setup is presented below as an example of an instrumental report:



```
Det 166 Results
Name                                              Area           Cl2, Mol/L
CLORINE                                       16320031                1.051

Totals
                                              16320031                1.051
```

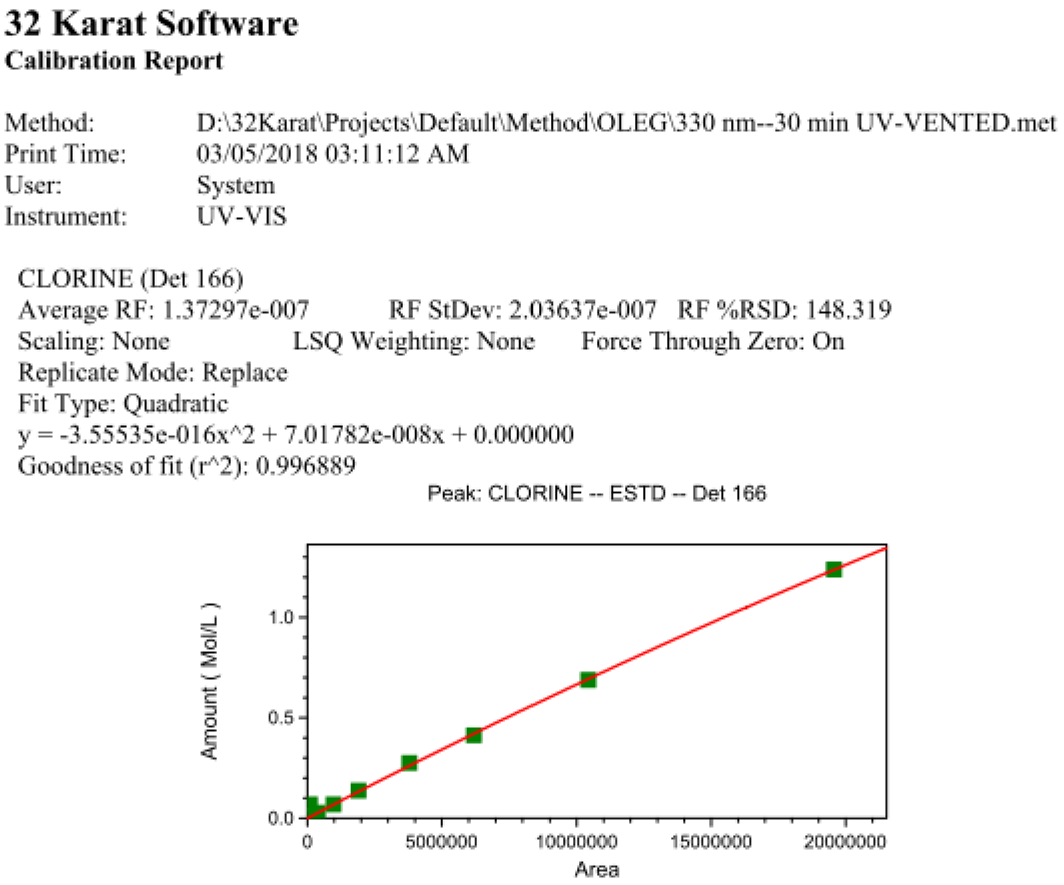
Fig. 11 Example of vented setup chlorine signal curve and its processing result (area and concentration).

The green trace is the chlorine signal curve and the red line is the baseline where integration was performed.

3.2.6. Vented setup calibration and validation

Several important analytical validation parameters of the vented setup such as sensitivity, linearity, repeatability, limit of detection, limit of quantitation, intermediate precision and range of concentrations were measured.

As mentioned above, the analytical signal of the closed setup was in optical adsorption units mAu and, the concentration of chlorine could be easily calculated (in Mol/L) for each time point of the curve. Unlike the closed setup the vented setup produced a chlorine curve in mAu units; however the entire curve is required for the calculation of a single result – the total chlorine concentration that is released. The total chlorine concentration is proportional to the area between chlorine signal curve and baseline. The area between baseline and chlorine signal curve was calculated by integration of chlorine signal curve using the chromatographic software. However, to convert the obtained area value into chlorine concentration a calibration of the vented setup was required. The vented setup was calibrated by separate runs with the injection of a single precisely known dose of chlorine by run; the dose was different in each run: 5, 10, 20, 50, 100, 200, 300, 500, 900 mL of pure chlorine. Therefore, in those 9 runs, 9 chlorine signal curves were obtained and the area under each curve was found by integration. Then, the calibration plot, which represented the relationship between the area under the signal curve and the chlorine concentration was made and as a result, the calibration parameters were calculated. Those operations were done using the chromatographic software 32 Karat from Beckman:



32 Karat Software

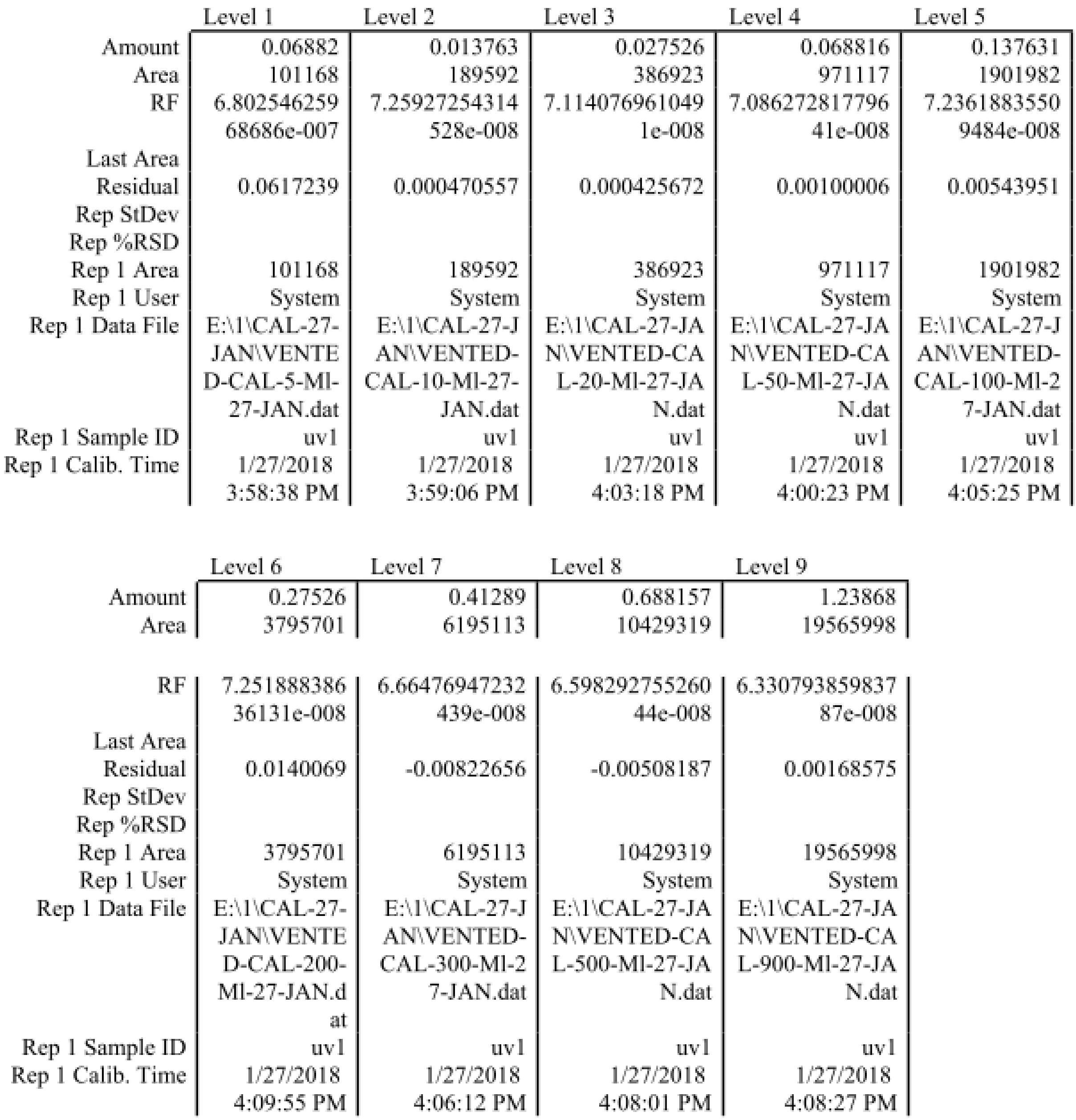
Calibration Report

Method: D:\32Karat\Projects\Default\Method\OLEG\330 nm--30 min UV-VENTED.met
Print Time: 03/05/2018 03:11:12 AM
User: System
Instrument: UV-VIS

CLORINE (Det 166)
Average RF: 1.37297e-007 RF StDev: 2.03637e-007 RF %RSD: 148.319
Scaling: None LSQ Weighting: None Force Through Zero: On
Replicate Mode: Replace
Fit Type: Quadratic
y = -3.55535e-016x^2 + 7.01782e-008x + 0.000000
Goodness of fit (r^2): 0.996889

Peak: CLORINE -- ESTD -- Det 166

(Continued below)



	Level 1	Level 2	Level 3	Level 4	Level 5
Amount	0.06882	0.013763	0.027526	0.068816	0.137631
Area	101168	189592	386923	971117	1901982
RF	6.80254625968686e-007	7.25927254314528e-008	7.1140769610491e-008	7.08627281779641e-008	7.23618835509484e-008
Last Area					
Residual	0.0617239	0.000470557	0.000425672	0.00100006	0.00543951
Rep StDev					
Rep %RSD					
Rep 1 Area	101168	189592	386923	971117	1901982
Rep 1 User	System	System	System	System	System
Rep 1 Data File	E:\1\CAL-27-JAN\VENTED-CAL-5-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-10-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-20-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-50-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-100-Ml-27-JAN.dat
Rep 1 Sample ID	uv1	uv1	uv1	uv1	uv1
Rep 1 Calib. Time	1/27/2018 3:58:38 PM	1/27/2018 3:59:06 PM	1/27/2018 4:03:18 PM	1/27/2018 4:00:23 PM	1/27/2018 4:05:25 PM

	Level 6	Level 7	Level 8	Level 9
Amount	0.27526	0.41289	0.688157	1.23868
Area	3795701	6195113	10429319	19565998
RF	7.25188838636131e-008	6.66476947232439e-008	6.59829275526044e-008	6.33079385983787e-008
Last Area				
Residual	0.0140069	-0.00822656	-0.00508187	0.00168575
Rep StDev				
Rep %RSD				
Rep 1 Area	3795701	6195113	10429319	19565998
Rep 1 User	System	System	System	System
Rep 1 Data File	E:\1\CAL-27-JAN\VENTED-CAL-200-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-300-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-500-Ml-27-JAN.dat	E:\1\CAL-27-JAN\VENTED-CAL-900-Ml-27-JAN.dat
Rep 1 Sample ID	uv1	uv1	uv1	uv1
Rep 1 Calib. Time	1/27/2018 4:09:55 PM	1/27/2018 4:06:12 PM	1/27/2018 4:08:01 PM	1/27/2018 4:08:27 PM

Fig. 12. The calibration report of the vented setup by 32-Karat HPLC software

The other validation parameters for the vented setup were also obtained. The plot below demonstrates excellent repeatability in replicated experiments:

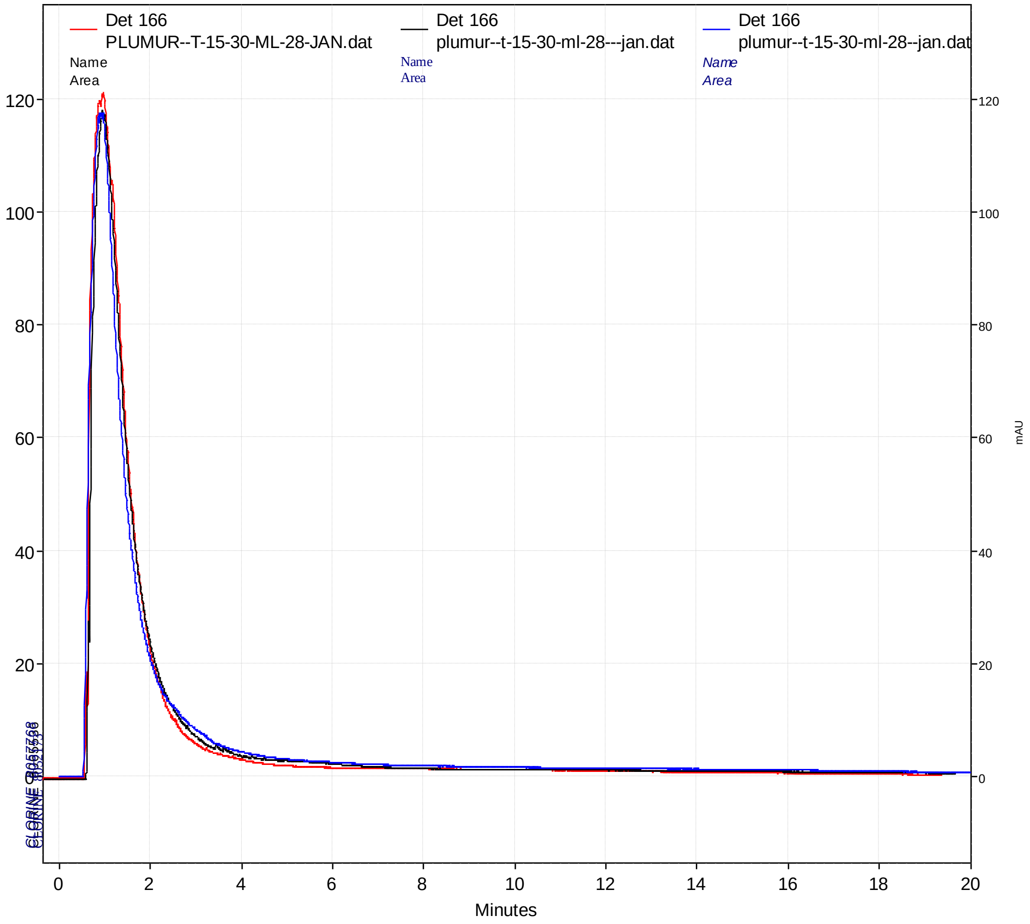


Fig. 13 Chlorine release from Liquid Plumr product at 15 °C in replicate experiments recorded using vented setup

3.2.7. Method validation parameters for vented setup:

- Range of quantification was determined as 4 orders of magnitude, from 4.46E-06 to 4.13E-02 Mol/L or 108 ppm (part per million, vol/vol) to 1,000,000 ppm chlorine, or the same 0.108% to 100% vol/vol of chlorine;
- The Limit of Quantification was determined as 4.46E-06 Mol/L of chlorine in air;
- Limit of detection was determined as 1.34E-06 Mol/L
- Repeatability was determined as RSD = 0.39%;
- Intermediate precision was determined as RSD = 0.86%
- Calibration curve fit was quadratic: $y = -3.555E\text{-}016x^2 + 7.0178E\text{-}008x$; the same as: $[Cl_2](Mol/L) = -3.555E\text{-}016\ (area)^2 + 7.0178E\text{-}008\ (area)$
- Method linearity was determined as $R^2 = 0.9969$
- Steering speed stability was determined as RSD = 0.002%

4. Results and discussions

4.1. Task 1: Calibration Curve Generation

4.1.1. Chlorine gas release during titration of sodium hypochlorite with hydrochloric acid

Conditions:

The experiments under Task 1 were conducted using the closed setup. In these experiments, 50 mL – aliquots of laboratory grade sodium hypochlorite of 8 different concentrations (15%; 12.1%; 9.6%; 7.2%; 4.8%; 2.4%; 1.2%, and 0%) were titrated by serial additions of 2 mL of 10% hydrochloric acid every 3 minutes for the maximum of 60 minutes time period. The time period of 0 to 3 minute, where no acid was added, was registered as the baseline.

During the course of the reactions, the amount of chlorine gas released and the change in the temperature of the reaction mixture were continuously measured. The pH of the reaction mixture was measured 1 minute after each acid addition. All experiments were conducted at 300 rpm (to reduce the equilibration time) at three different initial temperatures of 15, 22, and 30 °C.

The experiment was ended when no chlorine release was detected and the response curve formed a “plateau”.

Results:

Sodium hypochlorite solutions reacted with hydrochloric acid and the point of chlorine gas release was detected. The chlorine release curves at different temperatures are presented on the next 3 plots.

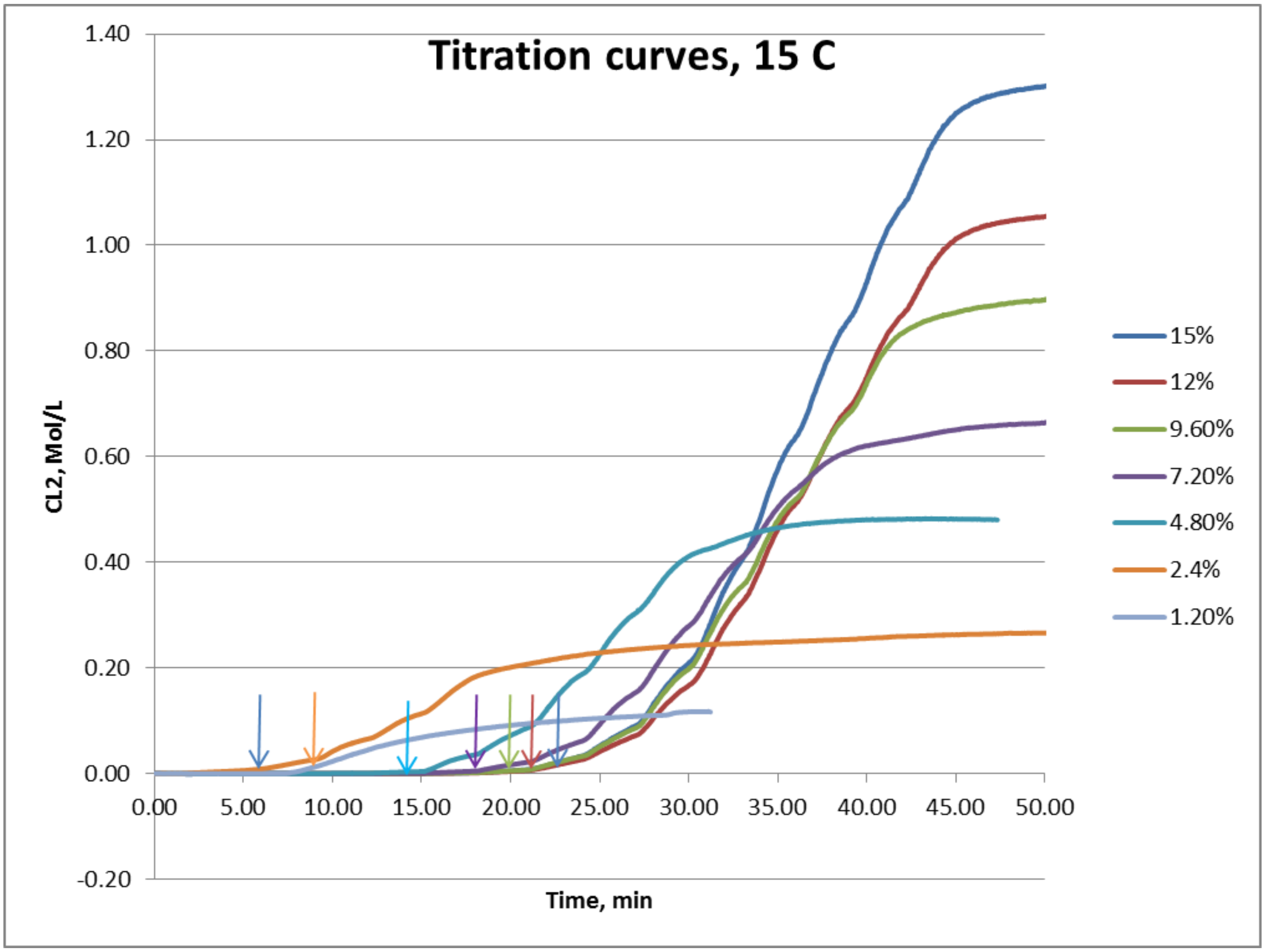


Fig. 14 Instrument plots of chlorine release at 15 °C during additions of 10% HCl, 2 mL of HCl added every 3 minutes, for different NaClO concentrations.

At 15 °C, an increase in NaClO solution concentration generally produced an increased amount of chlorine. At a certain amount of added HCl, no more chlorine was released; this resulted in a plateau on the curves. Therefore, more concentrated NaClO solutions required larger amounts of HCl to reach a “plateau”. Vertical arrows on the plot represent approximate time points where neutralization happened, and a chlorine release was detected. In the experiments it was noted, that initial pH of hypochlorite solution showed a slight decrease during preparation time and time required for temperature equilibration. This observation could be explained by the reaction of sodium hydroxide (present in sodium hypochlorite solution as a stabilizer) with atmospheric carbon dioxide. The time of solution preparation and equilibration was difficult to control, and this resulted in variability in the initial pH values and the positions of the neutralization points. However, the influence of carbon dioxide did not change the active chlorine concentration in hypochlorite solution and the total chlorine release. The neutralization points determined by pH~7 and the beginning of chlorine release will be compared a few pages below.

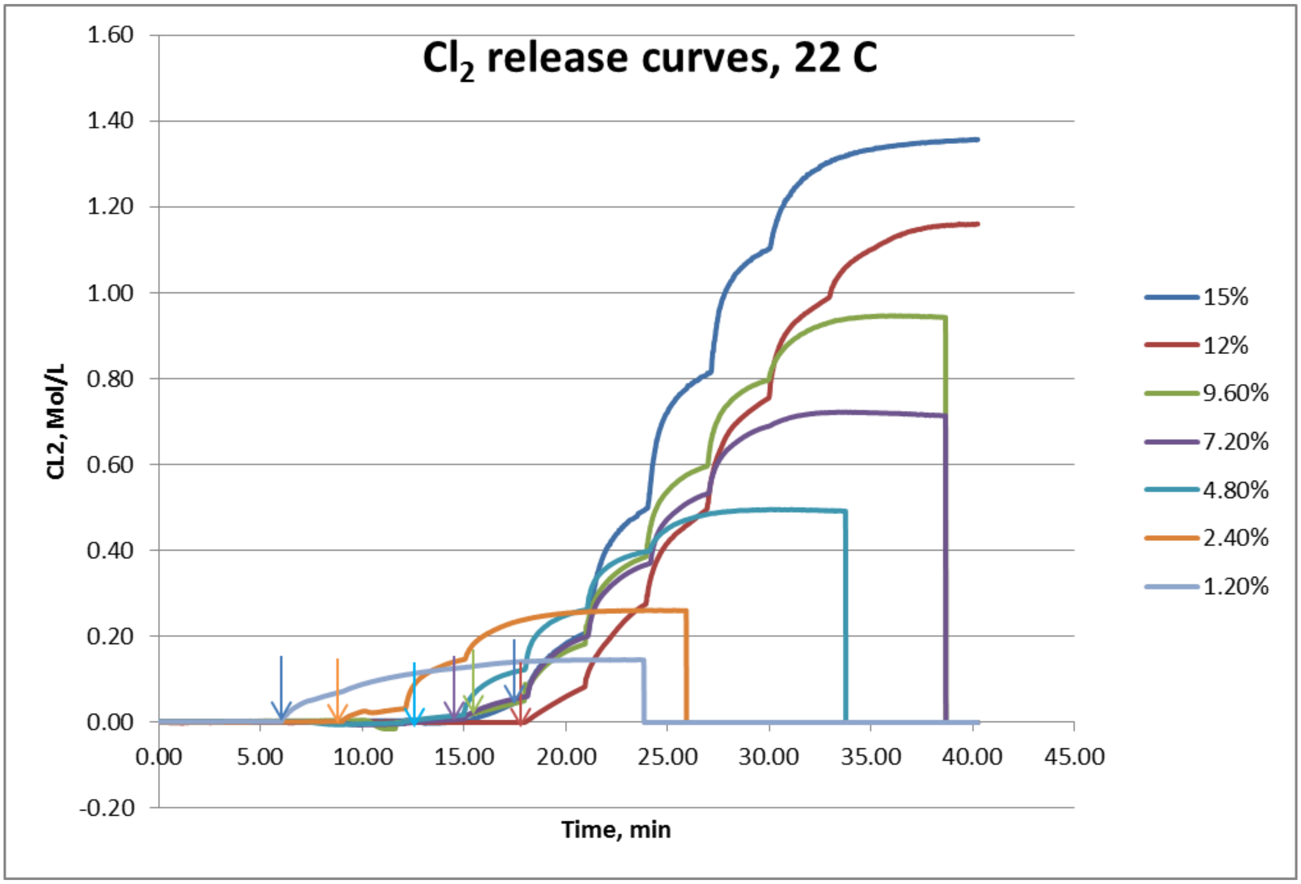


Fig. 15 Instrument plots of chlorine release at 22 °C during additions of 10% HCl, 2 mL of HCl every 3 minutes, for different NaClO concentrations.

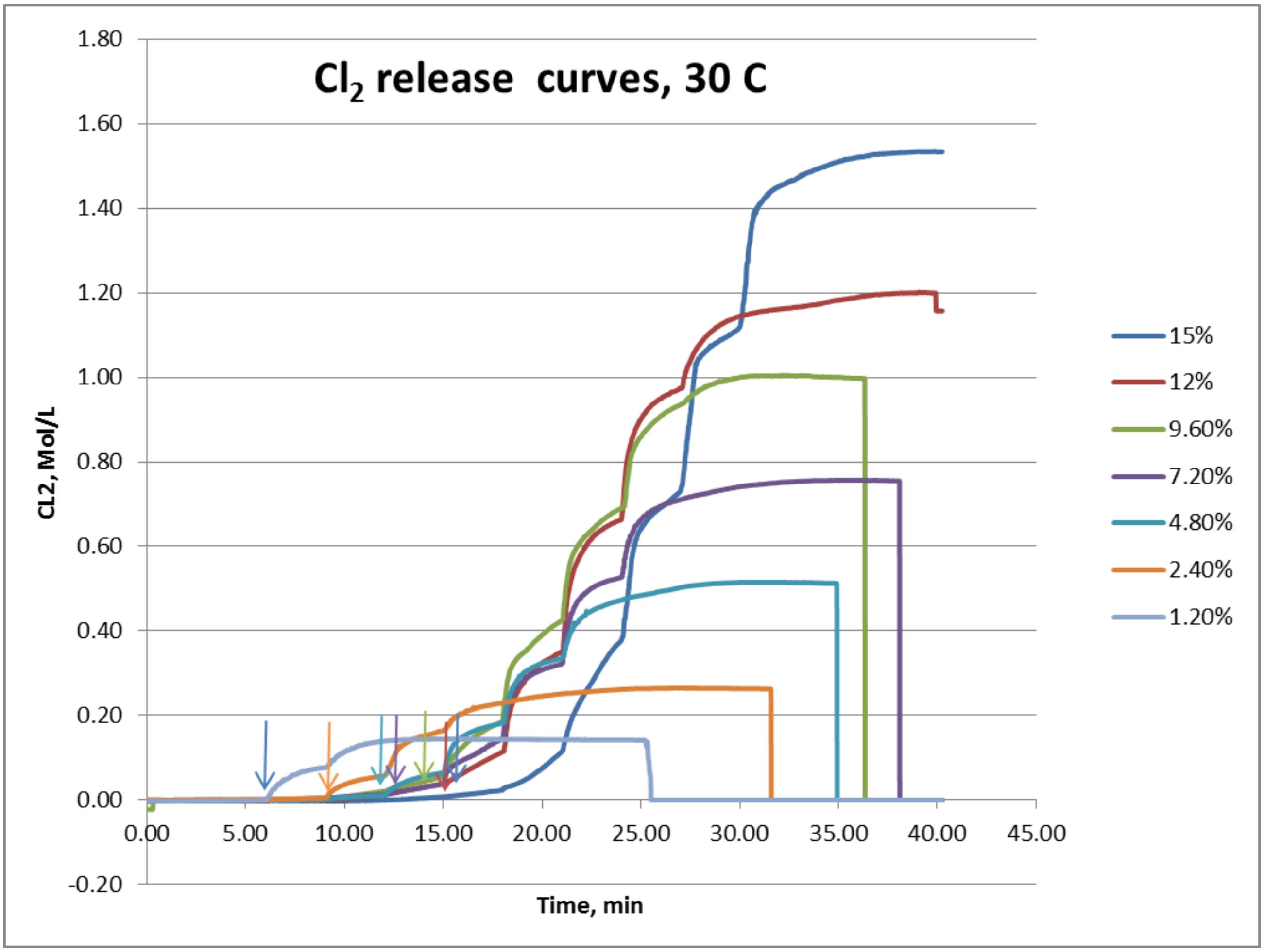


Fig. 16 Instrument plots of chlorine release at 30 °C during additions of 10% HCl, 2 mL of HCl every 3 minutes, for different NaClO concentrations.

For the plot above, please note the sharper bends of chlorine release curves and a higher level of the curve "plateaus" compared to the 22 °C plots and especially the 15 °C plots. This means that at higher temperatures, chlorine release was fastest and most intense.

The processed results of Task 1 include: volume of 10% HCl (mL) added to 1 L of sodium hypochlorite solution (ml/L: mL of HCl per L of NaClO), corresponding chlorine release (moles Cl_2 per 1 L NaClO = mol/L) and pH for eight NaClO concentrations (15% – to 0%) are presented in the tables below. The data in the tables below have a time increment of exactly 3 min between rows.

Table 5. Sodium hypochlorite titration results at 15 °C

Temperature: 15 °C

	15% NaClO		12.1% NaClO		9.6% NaClO		7.2% NaClO	
HCl mL/L	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH
0	0.000	13.5	0.000	13.23	0.000	12.53	0.000	13.22
40	0.000	12.9	0.000	11.72	0.000	12.08	0.000	9.28
80	0.001	10.51	0.000	9.17	0.000	10.22	0.000	8.54
120	0.001	9.33	0.000	8.75	0.000	7.69	0.000	8.11
160	0.002	8.88	0.000	8.35	0.001	7.302	0.001	7.67
200	0.003	8.54	0.001	8.01	0.002	6.82	0.004	7.12
240	0.011	8.02	0.005	7.47	0.006	6.24	0.019	6.15
280	0.047	6.52	0.023	6.81	0.029	5.36	0.056	4.48
320	0.142	5.36	0.065	5.23	0.079	4.51	0.143	4.13
360	0.339	4.96	0.155	4.62	0.185	4.21	0.263	3.96
400	0.584	4.51	0.303	4.15	0.338	3.85	0.395	3.59
440	0.827	4.12	0.491	3.84	0.503	2.98	0.523	2.35
480	1.057	3.57	0.673	3.24	0.664	1.85	0.603	1.41
520	1.186	2.79	0.848	2.47	0.820	0.95	0.630	0.96
560	1.239	1.81	0.996	1.53	0.869	0.76	0.649	0.76
600	1.255	1.25	1.044	0.98	0.888	0.64	0.660	0.71
640	1.256	0.92	1.056	0.75	0.899	0.52	0.665	0.62
680			1.067	0.55	0.902	0.47	0.666	0.501
720			1.071	0.31			0.666	0.43

(Table continued on the next page)

Table 6. Sodium hypochlorite titration results at 15 °C

Temperature: 15 °C

	4.8% NaClO		2.4% NaClO		1.2% NaClO		0% NaClO	
HCl mL/L	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH
0	0.000	13.04	0.000	12.8	0.000	11.73	0	5.04
40	0.000	8.75	0.008	8.26	0.000	7.07	0	1.27
80	0.000	8.11	0.024	7.34	0.008	2.81	0	1.01
120	0.001	7.65	0.062	4.41	0.040	1.49	0	0.96
160	0.004	6.88	0.108	3.49	0.066	1.15	0	0.84
200	0.033	4.84	0.174	2.64	0.082	0.94	0	0.52
240	0.080	4.45	0.205	1.37	0.093	0.78	0	0.41
280	0.177	4.01	0.223	1.04	0.102	0.68	0	0.32
320	0.291	3.52	0.234	0.93	0.108	0.58	0	0.21
360	0.400	2.15	0.242	0.78	0.116	0.42	0	0.11
400	0.442	1.17	0.246	0.72	0.116	0.31	0	0.1
440	0.468	0.92	0.250	0.61				
480	0.478	0.75	0.254	0.52				
520	0.482	0.62	0.259	0.50				
560	0.482	0.56	0.262	0.47				
600	0.480	0.53	0.265	0.43				

Table 7. Sodium hypochlorite titration results at 22 °C

Temperature: 22 °C

	15% NaClO		12.1% NaClO		9.6% NaClO		7.2% NaClO	
HCl mL/L	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH
0	0.000	12.71	0.000	13.28	0.000	13.21	0.000	10.91
40	0.002	9.22	0.001	11.88	0.003	9.51	0.000	8.94
80	0.003	8.64	0.001	9.02	0.004	8.63	0.001	8.1
120	0.004	8.18	0.001	8.51	0.006	8.14	0.001	7.65
160	0.001	7.68	0.001	8.11	0.010	7.62	0.007	6.42
200	0.046	6.64	0.042	7.63	0.045	6.72	0.055	5.12
240	0.198	5.36	0.073	6.35	0.175	4.73	0.190	3.65
280	0.480	4.22	0.262	4.85	0.378	3.44	0.359	2.74
320	0.797	3.1	0.480	3.95	0.589	2.07	0.524	1.93
360	1.089	2.13	0.741	2.82	0.790	0.95	0.683	1.01
400	1.294	0.95	0.975	1.82	0.924	0.77	0.720	0.71
440	1.338	0.78	1.114	1.2	0.946	0.61	0.720	0.49
480	1.352	0.62	1.156	0.96	0.943	0.44	0.714	0.38
520	1.359	0.54	1.157	0.35				
560	1.361	0.41	1.158	0.22				
600	1.359	0.33						

Temperature: 22 °C

	4.8% NaClO		2.4% NaClO		1.2% NaClO		0% NaClO	
HCl mL/L	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH
0	0.000	12.7	0.000	12.3	0.000	12.1	0	6.2
40	0.003	8.3	0.001	7.12	0.002	6.91	0	1.3
80	0.004	7.62	0.002	6.26	0.066	2.12	0	0.98
120	0.004	6.73	0.029	4.61	0.106	0.92	0	0.75
160	0.015	5.52	0.141	2.7	0.126	0.78	0	0.62
200	0.118	4.01	0.234	1.13	0.141	0.512	0	0.53
240	0.257	3.02	0.256	0.54	0.145	0.39	0	0.42
280	0.393	2.04	0.260	0.36	0.146	0.3	0	0.32
320	0.480	1.12	0.261	0.22			0	0.21
360	0.495	0.72					0	0.11
400	0.493	0.54					0	0.1
440	0.493							

Table 8. Sodium hypochlorite titration results at 30 °C

Temperature: 30 °C

	15% NaClO		12.1% NaClO		9.6% NaClO		7.2% NaClO	
HCl mL/L	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH
0	0.000	13.2	0.000	12.9	0.000	12.9	0.000	12.7
40	0.000	12.68	0.000	11.3	0.000	9.37	0.001	8.86
80	0.000	11.4	0.001	8.61	0.003	8.32	0.004	8.11
120	0.000	9.84	0.009	8.16	0.017	7.84	0.012	7.63
160	0.006	8.32	0.034	7.57	0.049	7.15	0.034	6.52
200	0.020	7.95	0.102	6.49	0.175	5.12	0.132	4.75
240	0.094	6.3	0.337	4.56	0.409	4.03	0.316	3.98
280	0.351	5.11	0.653	3.62	0.677	3.45	0.520	3.21
320	0.710	4.11	0.962	2.85	0.923	2.67	0.704	1.84
360	1.101	3.45	1.135	0.78	0.995	0.64	0.737	0.65
400	1.431	2.36	1.163	0.23	1.004	0.27	0.752	0.36
440	1.451	1.02	1.186	0.21	0.998	0.122	0.756	0.2
480	1.461	0.65	1.199	0.2				

Temperature: 30 °C

	4.8% NaClO		2.4% NaClO		1.2% NaClO		0% NaClO	
HCl mL/L	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH	Cl_2 release mol/L	pH
0	0.000	12.49	0.000	12.12	0.000	11.73	0	6.12
40	0.000	8.29	0.001	7.7	0.000	6.84	0	1.11
80	0.002	7.69	0.004	6.84	0.074	2.67	0	0.98
120	0.010	6.87	0.054	3.48	0.136	1.24	0	0.74
160	0.061	4.33	0.157	2.52	0.144	0.78	0	0.61
200	0.177	3.57	0.225	1.25	0.143	0.52	0	0.52
240	0.329	3.17	0.248	0.77	0.143	0.39	0	0.41
280	0.467	1.67	0.260	0.52	0.142	0.28	0	0.3
320	0.498	0.71	0.265	0.38			0	0.21
360	0.514	0.43	0.264	0.29				
400	0.515	0.27	0.265	0.19				
440	0.515	0.16						

Tables above show that the amount of chlorine release increases with an increased temperature, an increase in added hydrochloric acid and increase of sodium hypochlorite concentration. The objectives of this task were to determine:

1 –) The maximal amount of HCl that is safe if mixed with sodium hypochlorite of certain concentration (i.e. does not result in release of substantial amount of chlorine into the air);

2) The maximal amount of chlorine that could be released into the atmosphere if sodium hypochlorite is reacted completely.

The solutions for the objectives of this study are presented in the following two graphs:

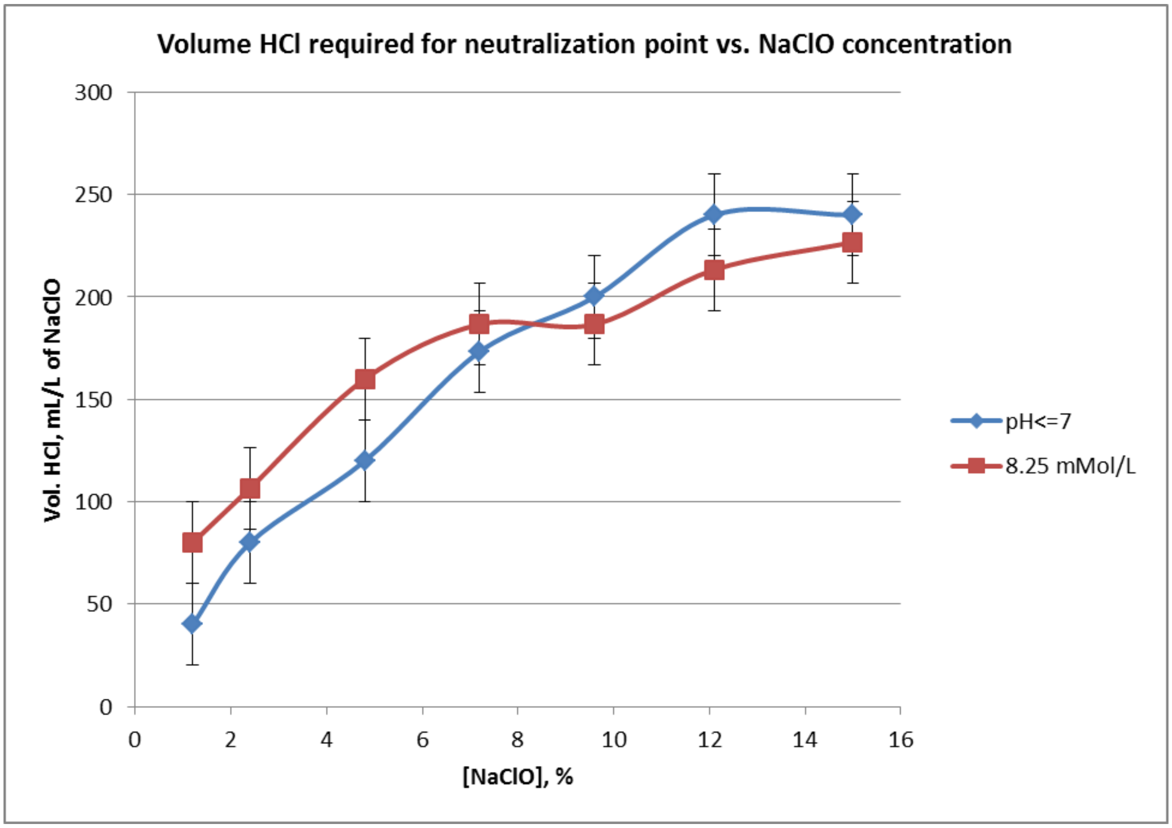


Fig. 17 Volume HCl required for neutralization point vs. NaClO concentration determined by pH<=7 and by beginning of chlorine release (8.25 mmol/L).

Based on the information obtained from the experiments and using two parameters, pH and beginning of chlorine release, the volume of 10% HCl that is required for neutralization of NaClO solutions at various concentrations was estimated. Since discrete HCl additions (2 mL) were made, the neutralization point was considered to be at pH<=7 (blue trace) and the beginning of chlorine release, was > 8.25 mMol/L (red trace in Fig. 17). The neutralization point and the beginning of chlorine release had little, if any, dependencies on the temperature. The two curves in Fig. 17 match with each other within an expected error range of ± 20 mL/L of HCl.

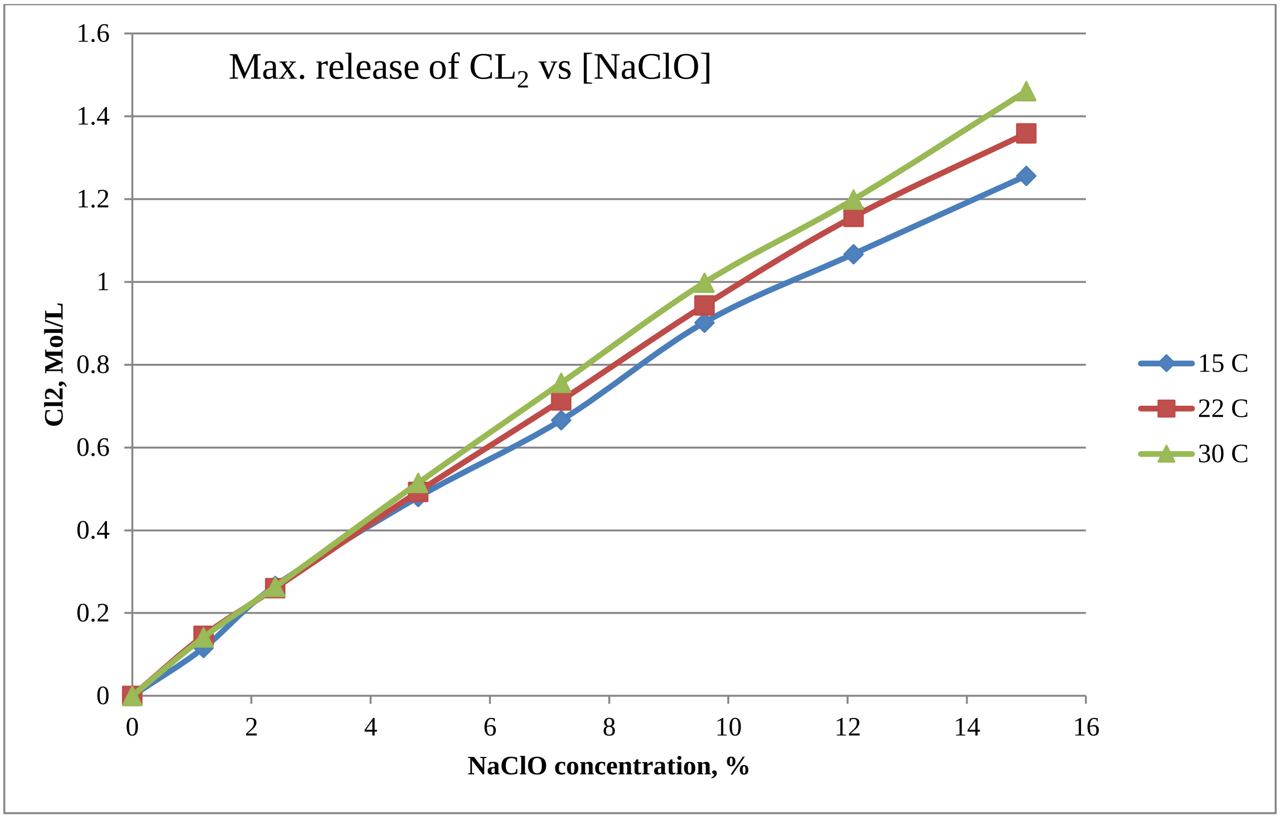


Fig. 18 “Maximum” release of chlorine from NaClO solutions of different concentrations at 15, 22 and 30 °C

Based on the results presented in Fig. 18, it can be concluded that if a product containing sodium hypochlorite were accidentally mixed with an excess of hydrochloric acid, then the amount of chlorine released after neutralization would be linearly proportional to the NaOCl concentration. In addition, the increase in the temperature also promotes more chlorine release.

4.1.2. Thermal effects during reaction of sodium hypochlorite with hydrochloric acid:

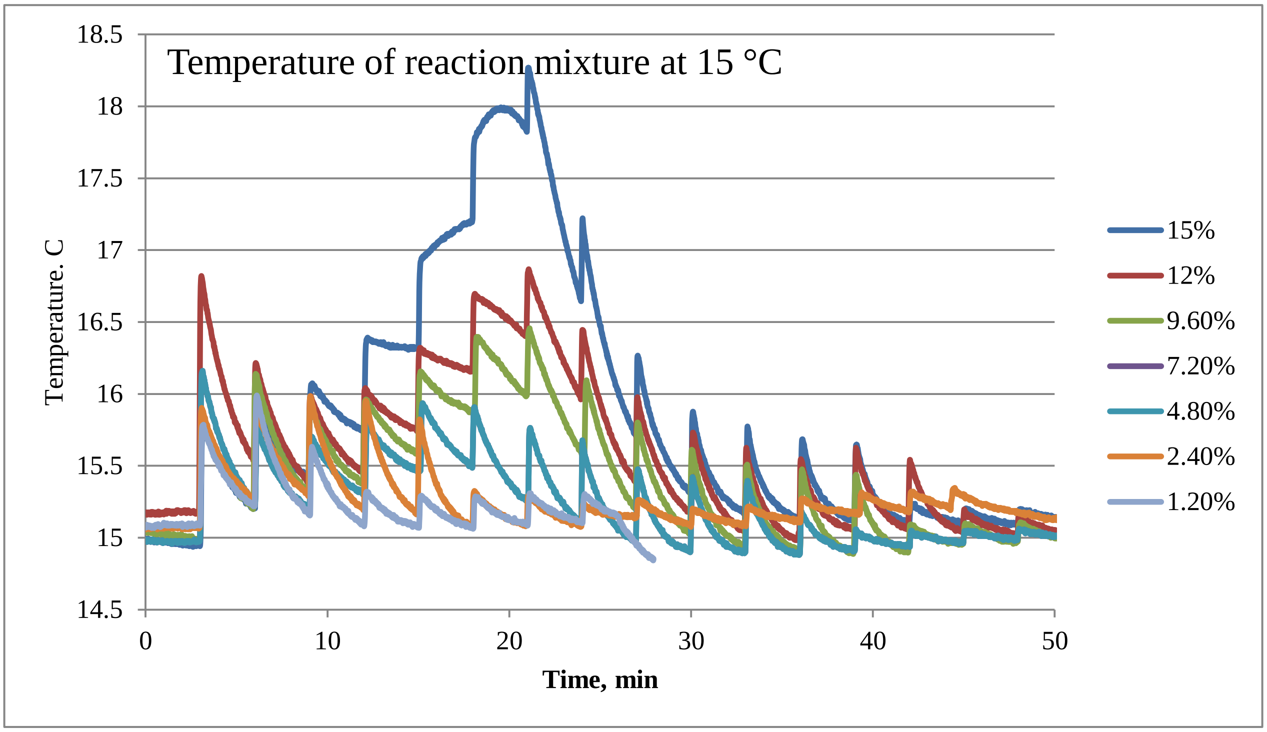


Fig. 19 Temperature recorded inside of liquid phase during titration of NaClO of different concentrations with 10% HCl at 15 °C initial temperature and 300 rpm.

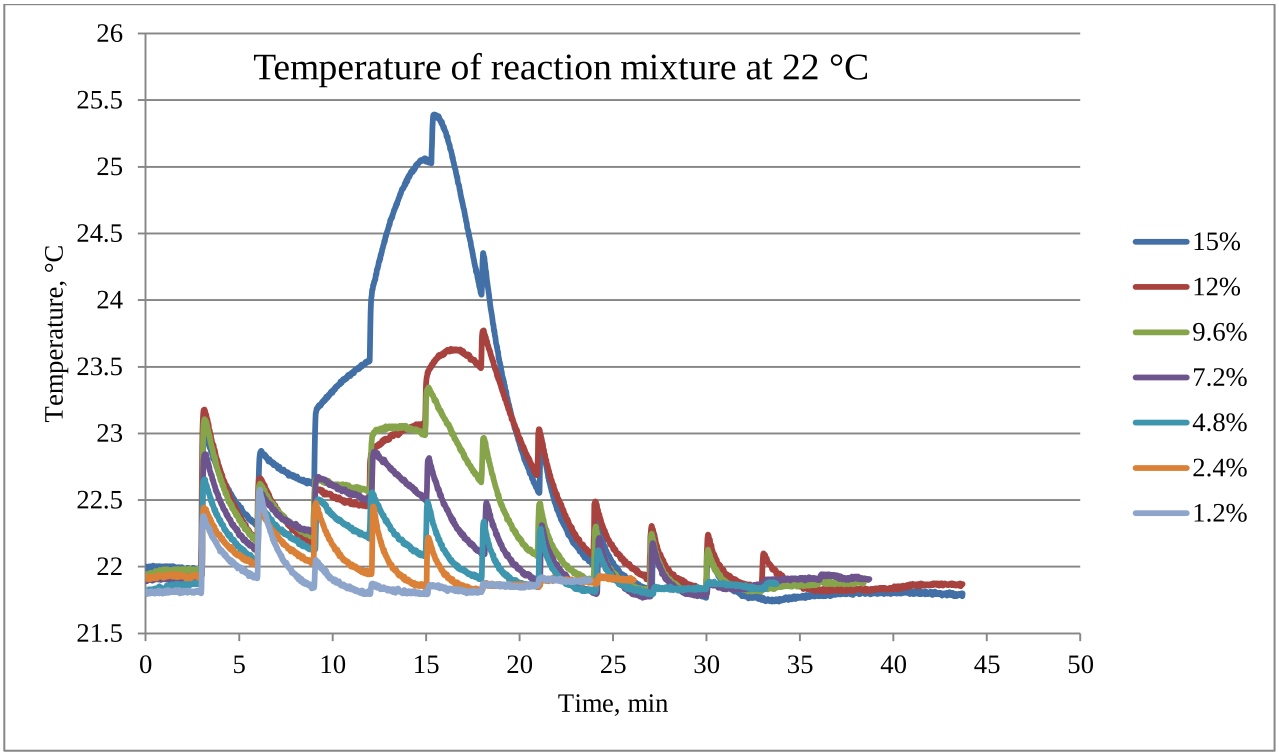


Fig. 20 Temperature recorded inside of liquid phase during titration of NaClO of different concentrations with HCl at 22 °C initial temperature and 300 rpm.

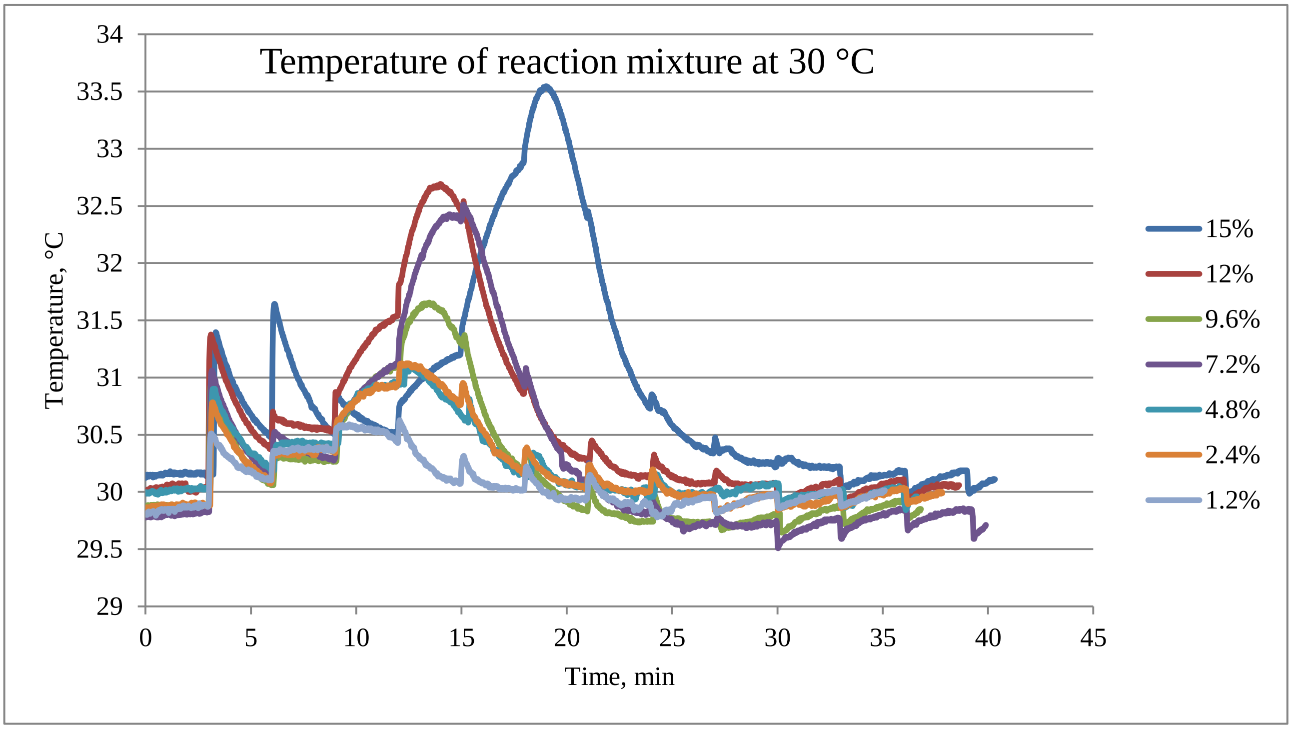


Fig. 21 Temperature recorded inside of liquid phase during titration of NaClO of different concentrations with HCl at 30 °C initial temperature and 300 rpm.

The thermal curves above are the results of direct temperature recording of reaction mixtures during NaClO titration experiments described above. Therefore, plots on Fig. 19 – 21 and on Fig. 14 – 16 correspond to one another, have the same timing of events and can be compared. In addition, the temperature curves can be compared with the appropriate lines of result tables. In conditions of the temperature controlled reactor, any heat released within it was recorded as a “peak”, so first raised temperature gradually lowers down to the thermostat’s temperature. The moments of HCl additions (addition of 2 mL of 10% HCl every 3 minutes) are clearly seen in the temperature curves. The first injection was done at 3 min, second at 6 min etc. First two peaks of heat release are most likely the results of the reaction of HCl with NaOH, then at times ~ 9 to 20 min. one can see the different shape of heat peaks, most likely this caused by formation of HClO out of ClO^- ions, those peaks are broad, and this reaction could be slower than HCl + NaOH. The following peaks (time from ~20 to 30 min) look narrower and deeper than two initial, this may due to several processes, including decomposition of HClO to Cl_2.

4.1.3. Chlorine gas release during titration of calcium hypochlorite with water

Conditions:

Within this part of Task 1, solid calcium hypochlorite (75%) was placed into the closed setup and mixed with different amounts of water at 3 different temperatures (15, 22, and 30 °C). The chlorine release and temperature of the reaction mixture were recorded continuously. The amount of added water was calculated based on desired concentrations of $Ca(ClO)_2$ vs. H_2O: 60%, 75%, 80%, 85%, 90%, 95% and 99% (Detailed calculations are in Appendix 4). For each experiment, 50 g of $Ca(ClO)_2$ was placed into the reactor, the system was closed, data acquisition initiated and only then the required amount of water (please see the Appendix 4) was added by injecting it inside of $Ca(ClO)_2$ powder through the Teflon capillary 11 (refer to Fig. 1).

The findings suggest, there was almost no chlorine that was released in the reactions of calcium hypochlorite with water at any of the 3 temperatures:

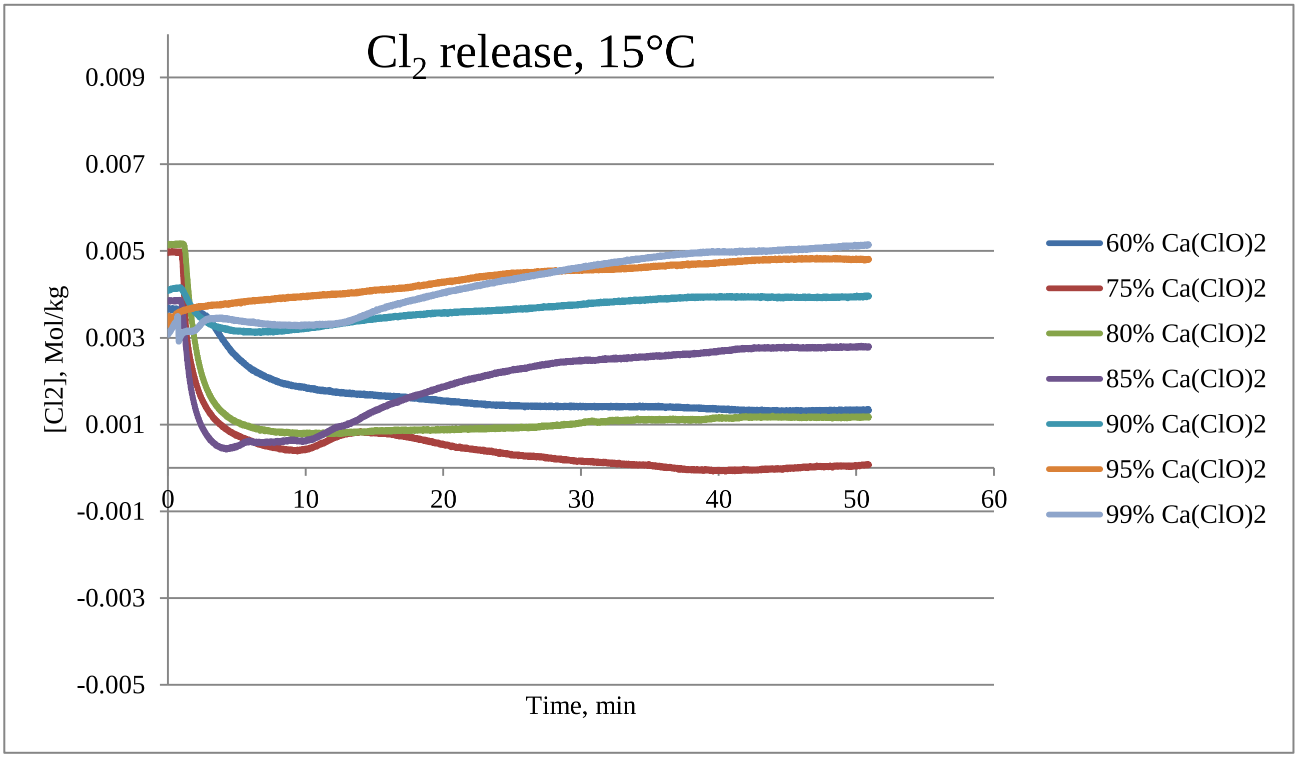


Fig. 22 Chlorine release during reaction of $Ca(ClO)_2$ with different amounts of water at 15 °C. Concentrations of aqueous calcium hypochlorite mixtures are given in the provided legend.

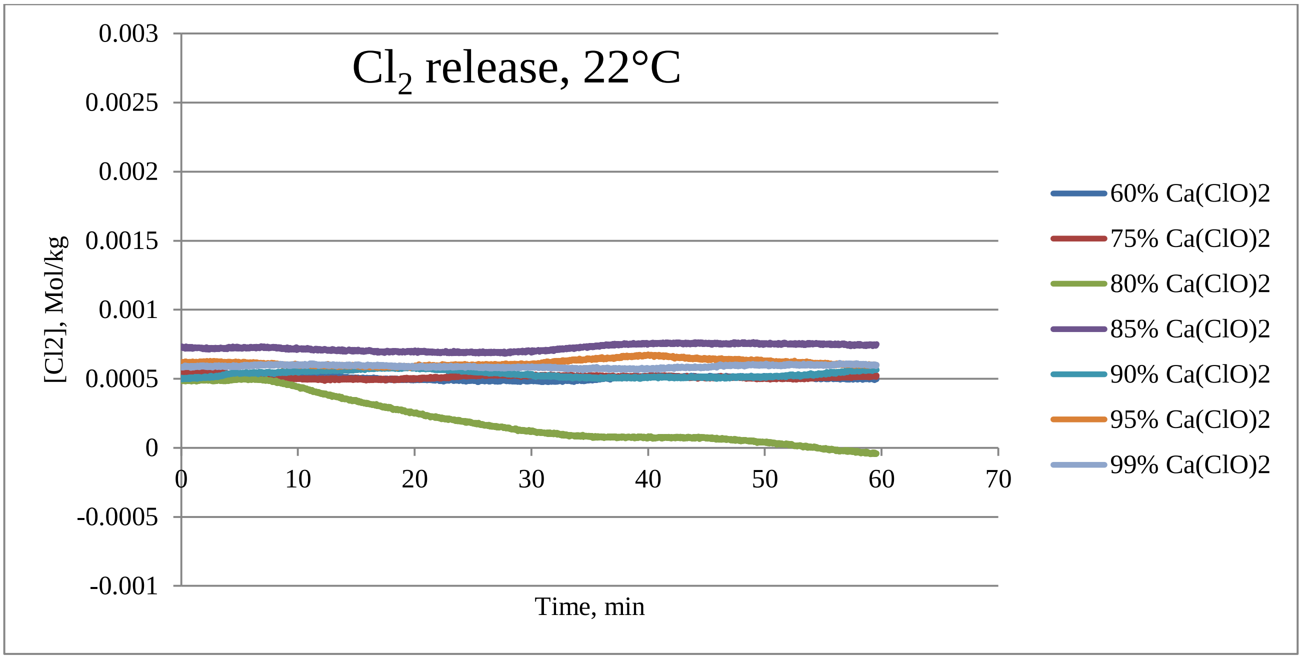


Fig. 23 Chlorine release during reaction of $Ca(ClO)_2$ with different amounts of water at 22 °C

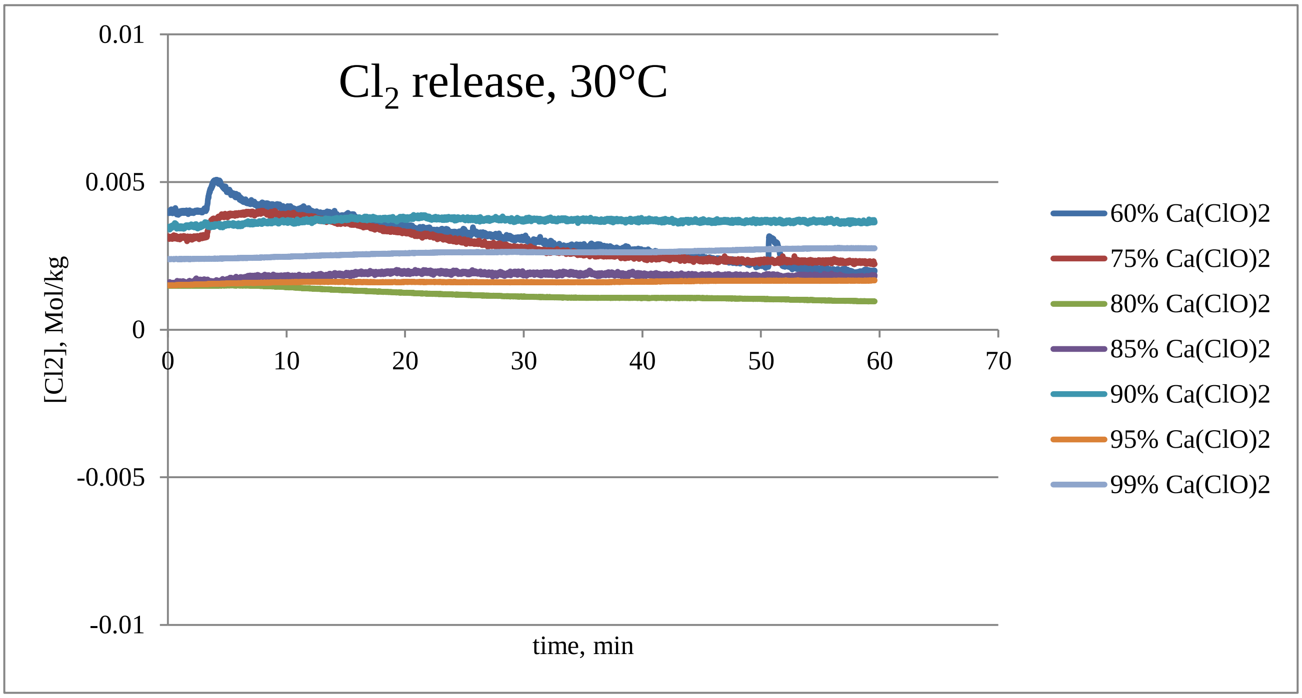


Fig. 24 Chlorine release during reaction of $Ca(ClO)_2$ with different amounts of water at 30 °C.

As illustrated in figures #22 to 24, there was no Cl_2 detection at 22 °C (the chlorine concentration curve remained horizontal, indicating no change in chlorine concentration within the setup); a slight increase of Cl_2 concentration was detected only for 95% and 99% concentrations of $Ca(ClO)_2$ at 15°C. Some decrease of background chlorine concentration was registered upon addition of water for the majority of the experiments at all temperatures.

The powder of $Ca(ClO)_2$ has some background concentration of chlorine gas in it, it was estimated (by the level of baselines) at approximately 3 to 5 mmol/kg depending on air exposure (refer to fig. 22 and fig. 24). The results of the experiments suggest that reaction of water with $Ca(ClO)_2$ results in a very slow chlorine release if there is a release at all:

$$Ca(OCl)_2 + H_2O \rightarrow Cl_2\uparrow + Ca(OH)_2 + \tfrac{1}{2}0_2\uparrow \qquad (4)$$

Small fluctuations of background chlorine concentration could be explained by physical factors. For instance, chlorine could be desorbed easier from granules at a higher temperature and at lower temperature background chlorine could be dissolved easier in injected water. In addition, fluctuations of background chlorine gas concentration could be caused by substantial heating of the reaction mixture, accompanied by water evaporation from mixture and condensation on reactor's walls. In the majority of the experiments, the temperature was raised from 10 to 15 °C above the initial temperature. Such thermal effects can be caused by hydration of $Ca(OCl)_2$. In addition, $Ca(OCl)_2$ contains some calcium oxide CaO (10-20%), which is known for its highly exothermic reaction with water:

$$CaO + H_2O \rightarrow Ca(OH)_2 \ \ (\Delta H_r = -65.2 \text{ kJ/mol at } 25\ ^\circ\text{C}) \ \ \text{(Chase, 1998)} \qquad (5)$$

The reaction of CaO and/or $Ca(OCl)_2$ with water and the resulting heat released did not promote decomposition of $Ca(OCl)_2$ and the release of chlorine gas in experimental conditions used within this study.

An example of heat release upon $Ca(OCl)_2$ reaction with water is shown on the plot below:

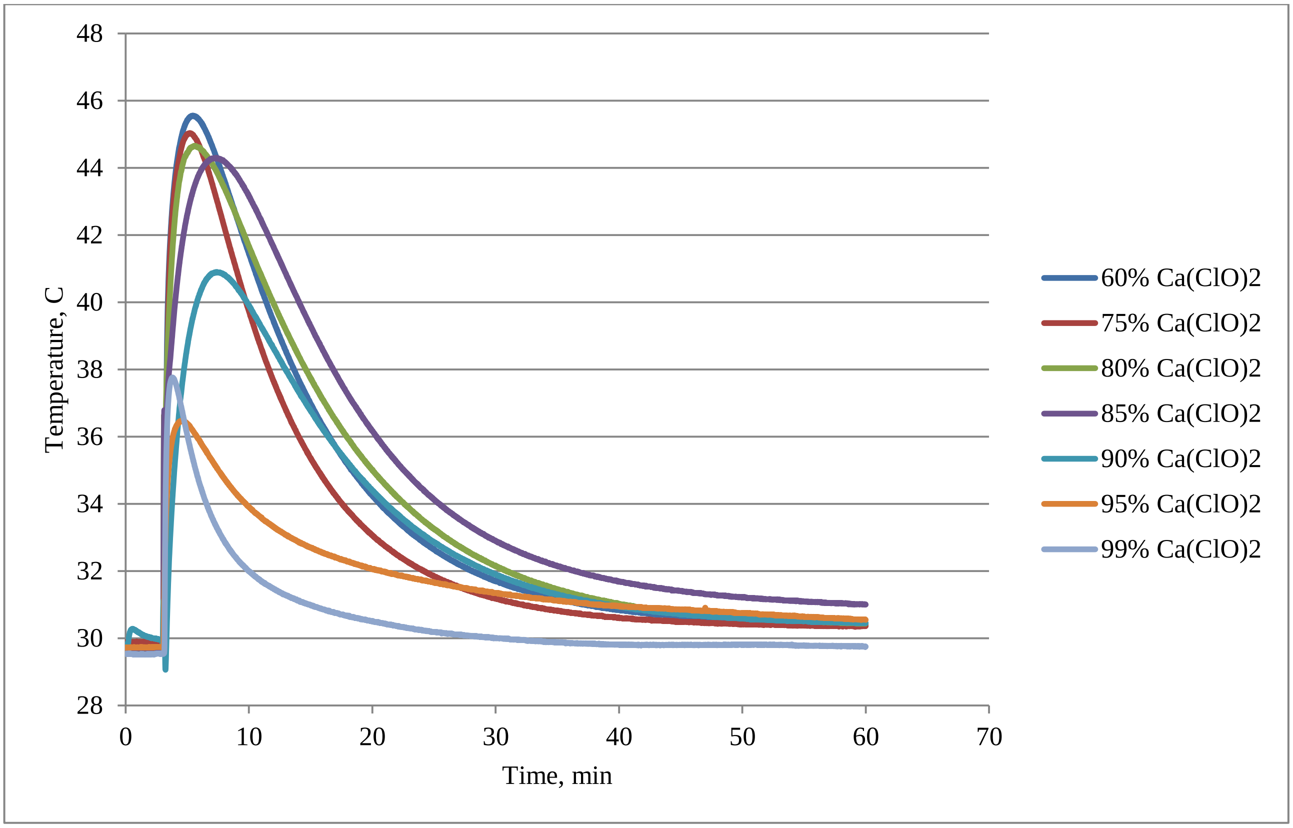


Fig. 25 Release of heat during reactions of calcium hypochlorite with water at different ratios. The initial temperature was 30 °C.

As the results of the present study suggest, the wetting of calcium hypochlorite with water shall not pose significant risk of chlorine gas release and there should not be any associated poisoning of users in such kind of accidents.

4.1.4. Conclusion for Task 1

Based on the information obtained within Task 1, the quantity of HCl required for neutralization of solutions of sodium hypochlorite is linearly related to the sodium hypochlorite concentration. Neutralization of sodium hypochlorite is accompanied with the beginning of chlorine release.

Chorine release from sodium hypochlorite mixed with an excess of hydrochloric acid was linearly proportional to the sodium hypochlorite concentration. An increased temperature also increases the chlorine release from sodium hypochlorite.

Calcium hypochlorite did not release chlorine in the reaction with water.

4.2. Task 2: Assessing Chlorine Release Efficiency

The objective of Task 2 was to determine chlorine release efficiency from 6 hypochlorite-based products. A hypochlorite product mixed with an acid or water could release some quantity of chlorine which can be less than theoretically expected because of a matrix effect. The matrix effect could be caused by reactions of different additives or impurities in a product with chlorine, such as chlorination of organic additives, for example, surfactants, thickeners and so on. As a result of such parallel reactions, the total chlorine release could be lower than expected based on the reaction stoichiometry.

In this task were used 3 liquid products, based on sodium hypochlorite:

1. Ultra San, by ECOLAB;
2. Javel 12, by SANY;
3. Liquid Plumr, by Cloro;

& 3 solid products:

4. Super Shock, by hth (Calcium Hypochlorite, 75%);
5. Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate, 100%);
6. Stabilized chlorinating pucks by hth (Trichloro-S- Triazinetrione, 100%).

In the first stage of this task, the active chlorine concentration was determined for each chlorination product (refer to the appropriate section in appendix 2) and, for each of products, the theoretical amount of released chlorine was calculated based on iodometric titration results and stoichiometry. The analysis was done using iodometric titration with potassium periodate as a primary standard (please see appendix 2).

Table 9. Iodometric titration results for 6 hypochlorite products

Product	**% Active Ingredient by Iodometric titration**	**% Active Ingredient as stated by manufacturer**	**Active Ingredient formula**
Javel 12, by SANY	10.44	12%	$NaClO$
Liquid Plumr, Clorox	5.22	N/A	$NaClO$
Ultra San, ECOLAB	11.73	N/A	$NaClO$
Super Shock hth	83.74	75%	$Ca(OCl)_2$
Stabilized chlorinating granules	91.22	100%	$C_3H_4Cl_2N_3NaO_5$
Stabilized chlorinating pucks	93.04	100%	$C_3Cl_3N_3O_3$

Expected chlorine release was calculated based on “active chlorine” stoichiometry. NaClO molecule has one active chlorine and therefore, it could release one chlorine molecule (Cl_2). $Ca(OCl)_2$ has two active chlorine atoms, and accordingly, it could release two chlorine molecules. The same rationale holds true for Sodium dichloro-s-triazinetrione dihydrate. The Trichloro-S- Triazinetrione has 3 active chlorines and in the appropriate conditions may release 3 molecules of chlorine. The active chlorine corresponds to chlorine that is in oxidation state +1 and if it reacts with Cl^- the product will be chlorine molecule Cl_2.

At the second stage of Task 2, the three liquid products (Javel-12, Liquid Plumr and Ultra San) were reacted with 10% hydrochloric acid and the three solid products (Super Shock, Stabilized chlorinating granules and Stabilized chlorinating pucks) were reacted with water at 3 different temperatures (15, 22 and 30 °C). The maximum quantity of chlorine released from each of the products was measured using two setups: the closed setup and the vented setup.

The obtained results were compared to the theoretically expected chlorine release and are summarized in the table below:

Table 10. Chlorine release efficiency in 1 hour experiment

			Detected Cl_2, release (mol/L)		Release efficiency	
Temp. °C	**Product name, (active ingredient) + Reactant**	**Expected Cl_2 release (mol/L)**	**Closed**	**Vented**	**Closed %**	**Vented %**
15	Ultra San, ECOLAB (NaCLO) + HCl	1.576	1.270	1.355	80.584	85.948
22	Ultra San, ECOLAB (NaCLO) + HCl	1.576	1.315	1.381	83.439	87.648
30	Ultra San, ECOLAB (NaCLO) + HCl	1.576	1.384	1.562	87.817	99.142
15	Javel 12, by SANY (NaCLO) + HCl	1.403	1.142	1.153	81.397	82.205
22	Javel 12, by SANY (NaCLO) + HCl	1.403	1.188	1.228	84.676	87.522
30	Javel 12, by SANY (NaCLO) + HCl	1.403	1.254	1.332	89.380	94.961
15	Liquid Plumr, Clorox (NaCLO) + HCl	0.702	0.585	0.629	83.333	89.540
22	Liquid Plumr, Clorox (NaCLO) + HCl	0.702	0.618	0.658	88.034	93.779
30	Liquid Plumr, Clorox (NaCLO) + HCl	0.702	0.651	0.661	92.735	94.174
15	Super Shock hth (Ca(OCL)2) + H_2O	11.72	0	0	0	0
22	Super Shock hth (Ca(OCL)2) + H_2O	11.72	0	0	0	0
30	Super Shock hth (Ca(OCL)2) + H_2O	11.72	0	0	0	0
15	Stabilized chlorinating pucks (TCA) + H_2O	12.005	0.0035	0	0.029	0
22	Stabilized chlorinating pucks (TCA) + H_2O	12.005	0.0089	0	0.074	0
30	Stabilized chlorinating pucks (TCA) + H_2O	12.005	0.0134	0	0.112	0
15	Stabilized chlorinating granules (NaDTA) + H_2O	7.127	0.0013	0	0.018	0
22	Stabilized chlorinating granules (NaDTA) + H_2O	7.127	0.001	0	0.014	0
30	Stabilized chlorinating granules (NaDTA) + H_2O	7.127	0.0023	0	0.032	0

4.3.0. Conclusion for Task 2

For the three liquid products, the chlorine release efficiency was in the range of 80 to 99% for the theoretically expected value. The chlorine release efficiency from liquid products also depends on the temperature such that at higher temperatures the efficiency is generally higher than that at the lower temperatures. A slightly higher chlorine release was measured using the vented setup in comparison to the closed setup. This was expected because the closed setup did not account chlorine, dissolved in the liquid reaction mixture. All liquid products completely reacted with hydrochloric acid within 5 to 10 minutes following the acid addition, so the time of the experiment was limited to 1-hour and this was more than enough for accurate measurement of total chlorine released. Obviously, all of the liquid products that were tested pose an extreme danger in case of accidental mixing with hydrochloric acid.

Unlike liquid products, solid products that were tested released only small amounts of chlorine during the period of the experiment, which was limited to 1-hour. The vented setup did not appear to be sensitive enough to measure such small quantities of released chlorine and so zeros were reported as results. The reactions between solid products and water were very slow and as a result, it was impossible to measure total chlorine that was released from solid products. One may note that in this study 3 liquid products were reacted with hydrochloric acid however 3 solid products were reacted with water. Hydrochloric acid will most likely also violently react with solid products causing extreme danger, but this was not included in the scope of the present study.

4.3. Task 3: Assessing the Speed of the Reaction

In Appendix 1 “Chemical Kinetics Background” the background information about chemical kinetics, detailed explanations of terms such as initial reaction rate, instantaneous reaction rate, maximal instantaneous reaction rate, t=0, and calculation principles are described. In this Appendix, the theoretical information and the practical applications directly related to the results obtained in the present study have been addressed. It is advised to read this Appendix before proceeding to the results of the tasks 3 and 4.

The objective of Task 3 was to assess the speed of the reaction of chlorine release from hypochlorite products.

Presented below is a traditional kinetic study using the first derivative of concentration/time data and a linear regression method with further Arrhenius parameter calculations. All of the initial data was obtained using the closed setup with a high stirring speed (300 rpm). A high stirring speed was required for the task 3 in order to avoid the dependence of the reaction rate from being affected by the diffusion of the reactants such that the reaction was controlled by thermodynamics. The dependence of reaction rates on diffusion (mixing) was studied under the task 4.

In Task 3, kinetic parameters for the reactions of 3 liquid hypochlorite products with 10% HCl and 3 solid products with water at 3 different temperatures (15, 22, and 30°C) was measured. The products are the same as used in Task 2. As a result, the Arrhenius parameters for each product were estimated.

4.3.1. Ultra San, by ECOLAB:

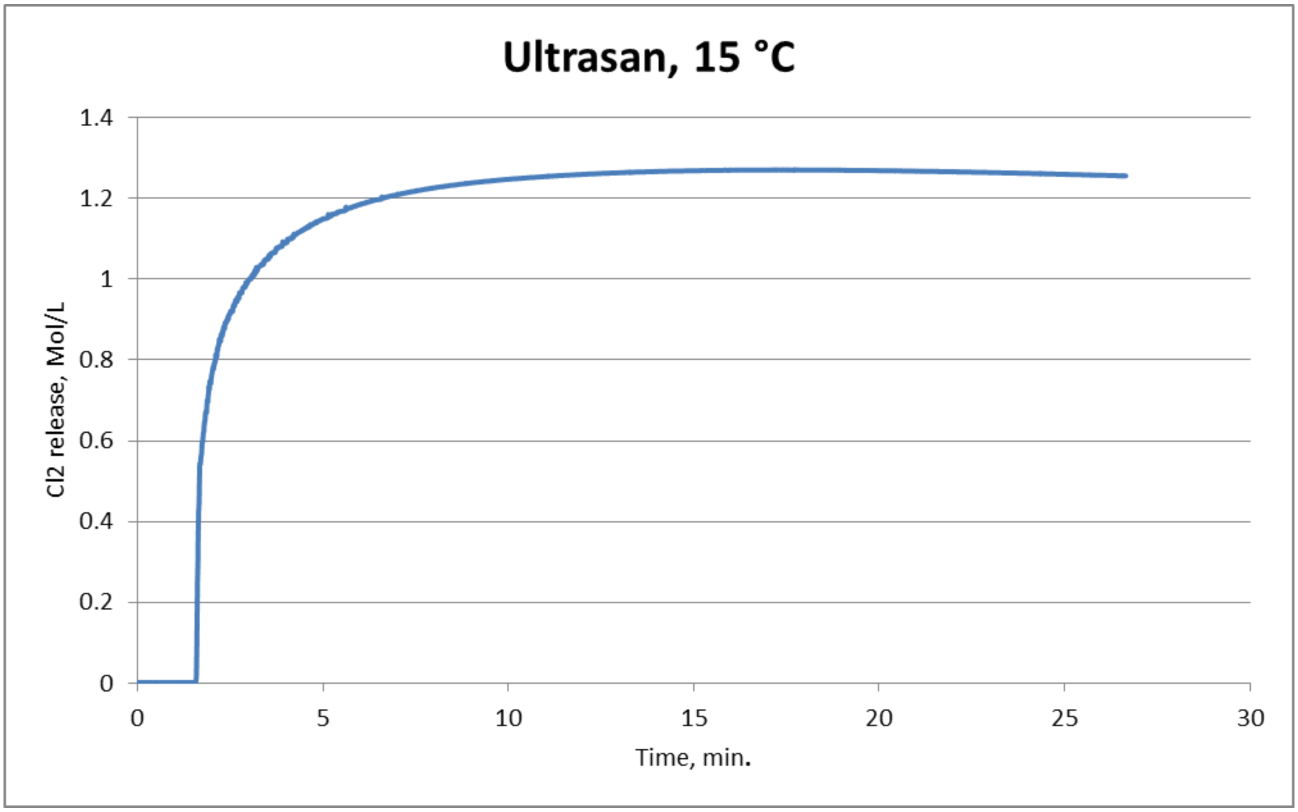


Fig. 26 Chlorine release from Ultra San product reacted with 10% HCl at 15 °C

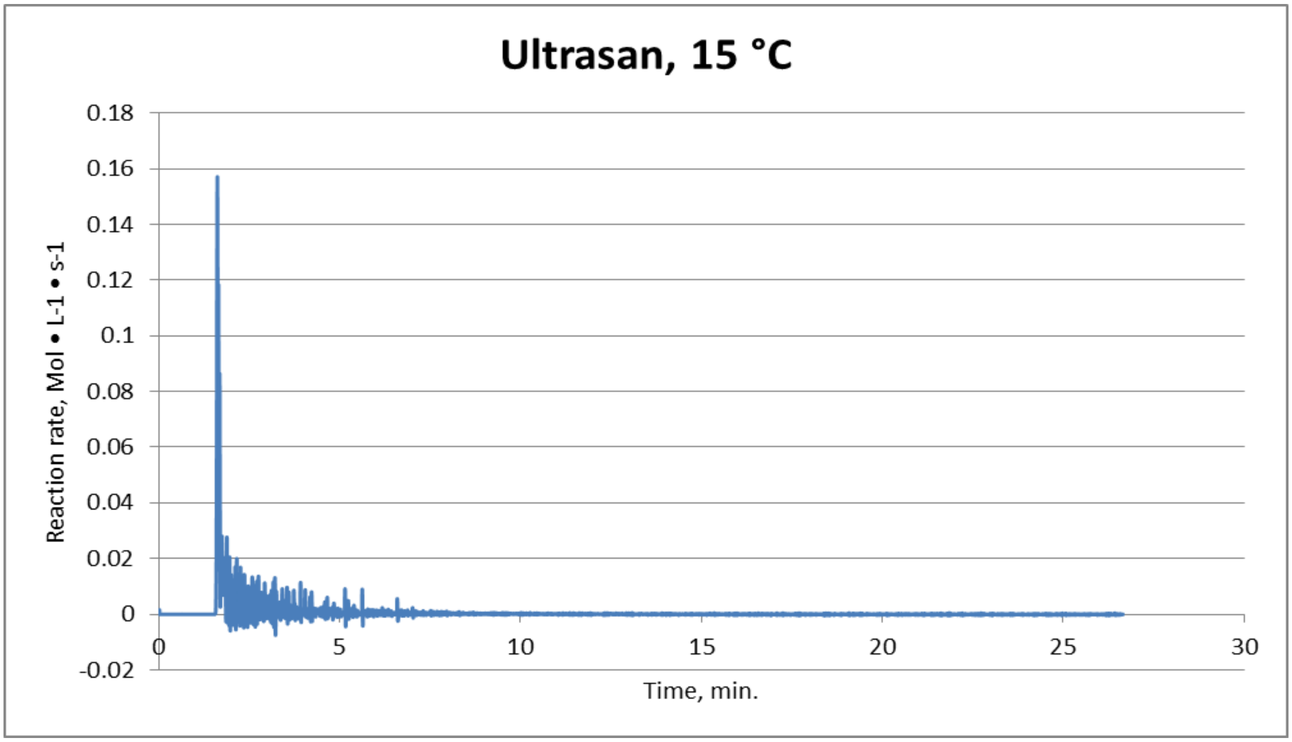


Fig. 27 Instantaneous rate of chlorine release from Ultra San product reacted with 10% HCl at 15 °C

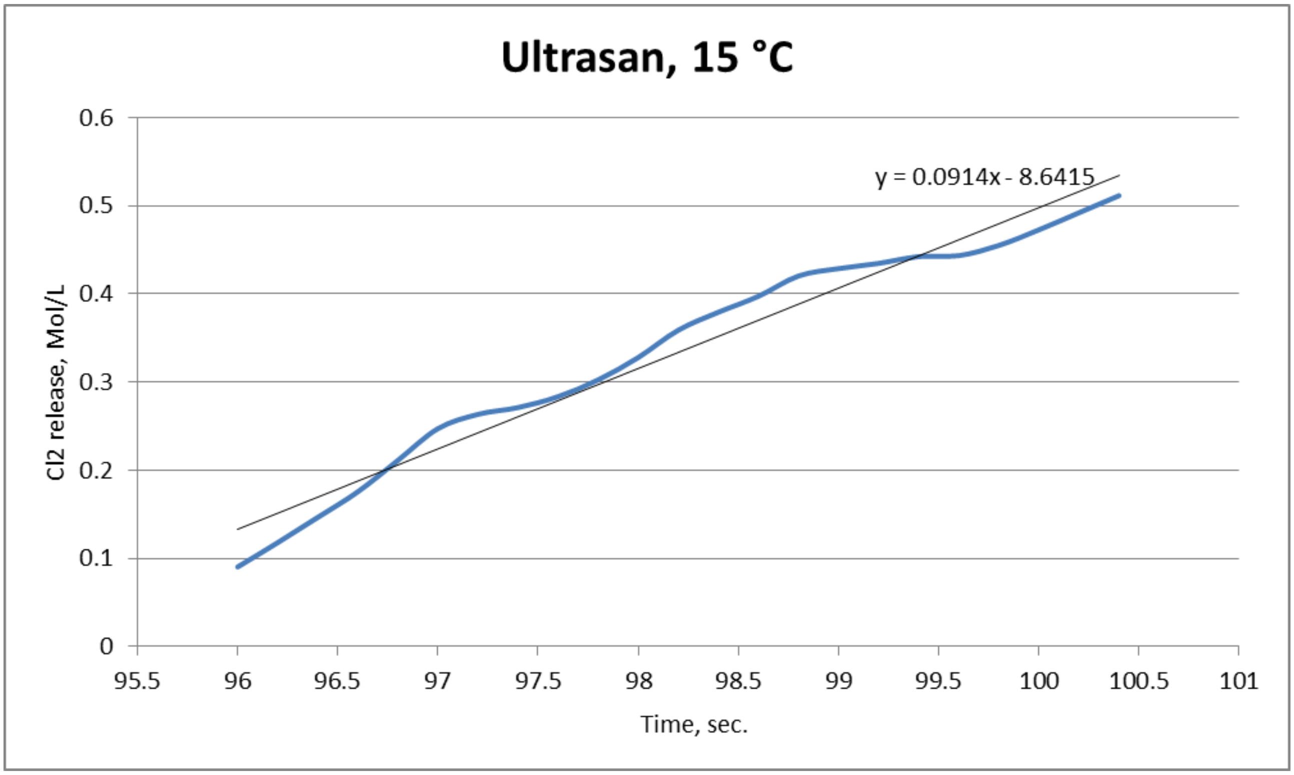


Fig. 28 Chlorine release from Ultra San product reacted with 10% HCl at 15 °C; part used for initial rate calculation.

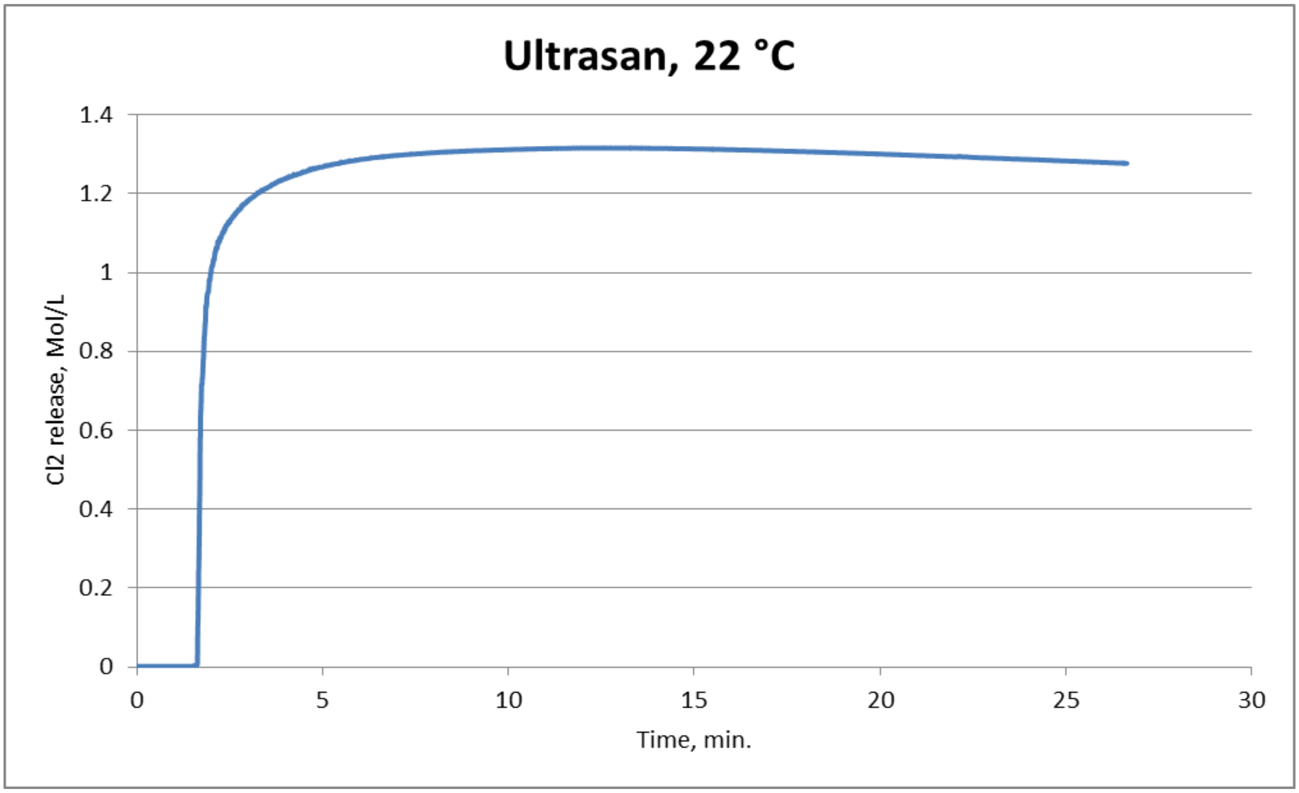


Fig. 29 Chlorine release from Ultra San product reacted with 10% HCl at 22 °C

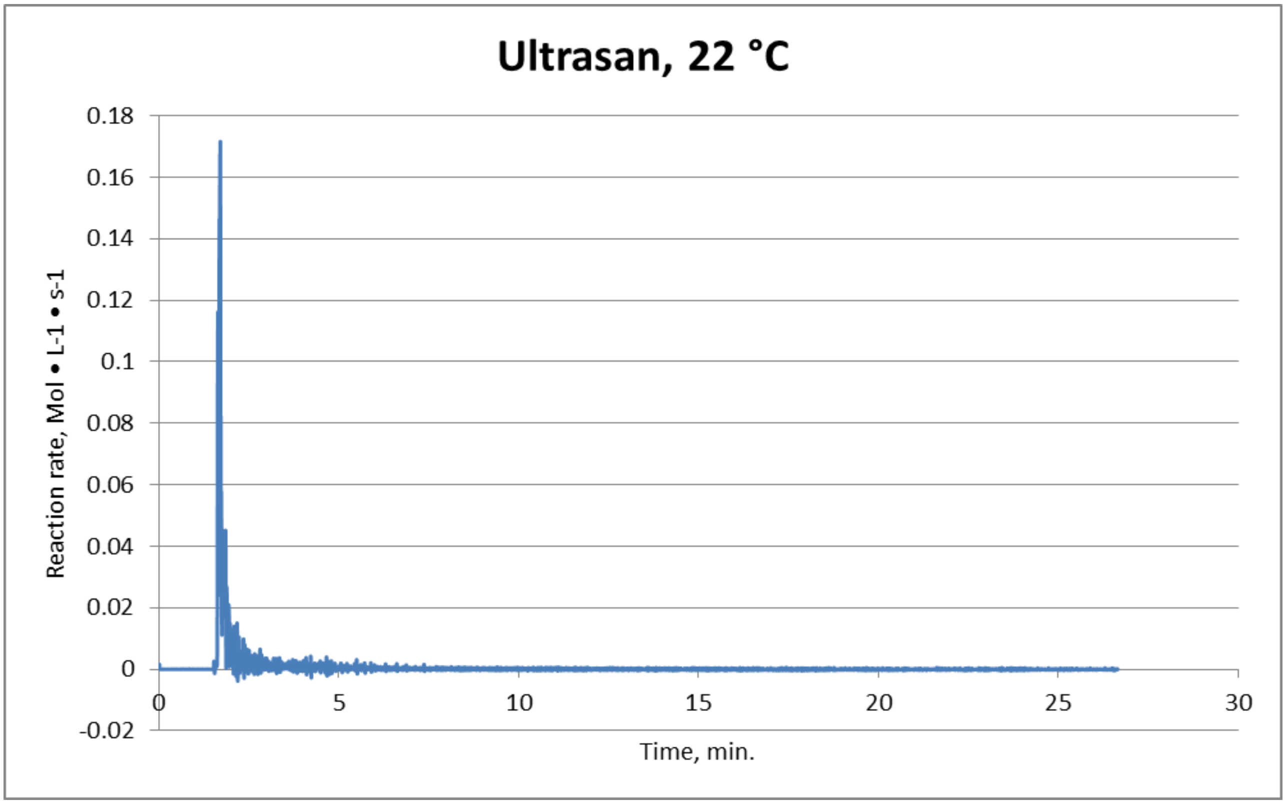


Fig. 30. Instantaneous rate of chlorine release from Ultra San product with 10% HCl at 22 °C

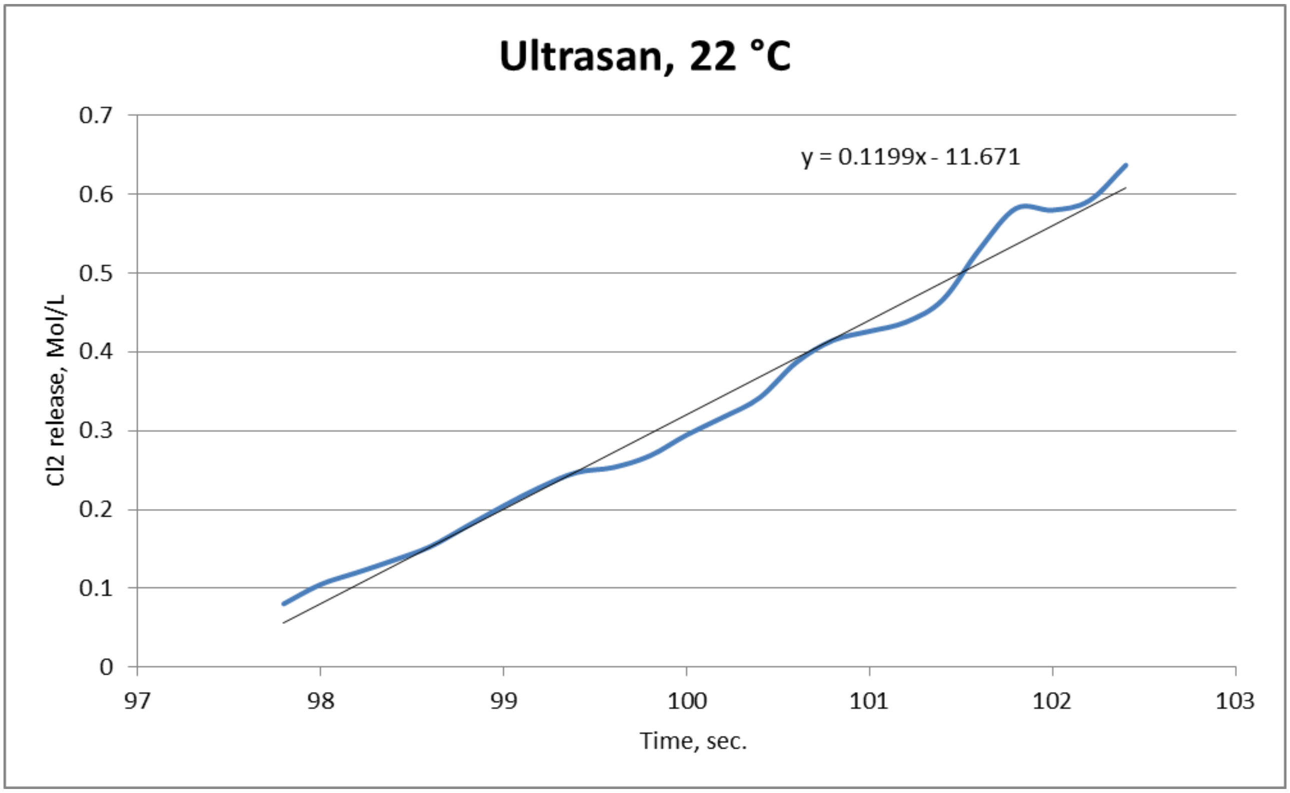


Fig. 31 Chlorine release from Ultra San product reacted with 10% HCl at 22 °C; part used for initial rate calculation.

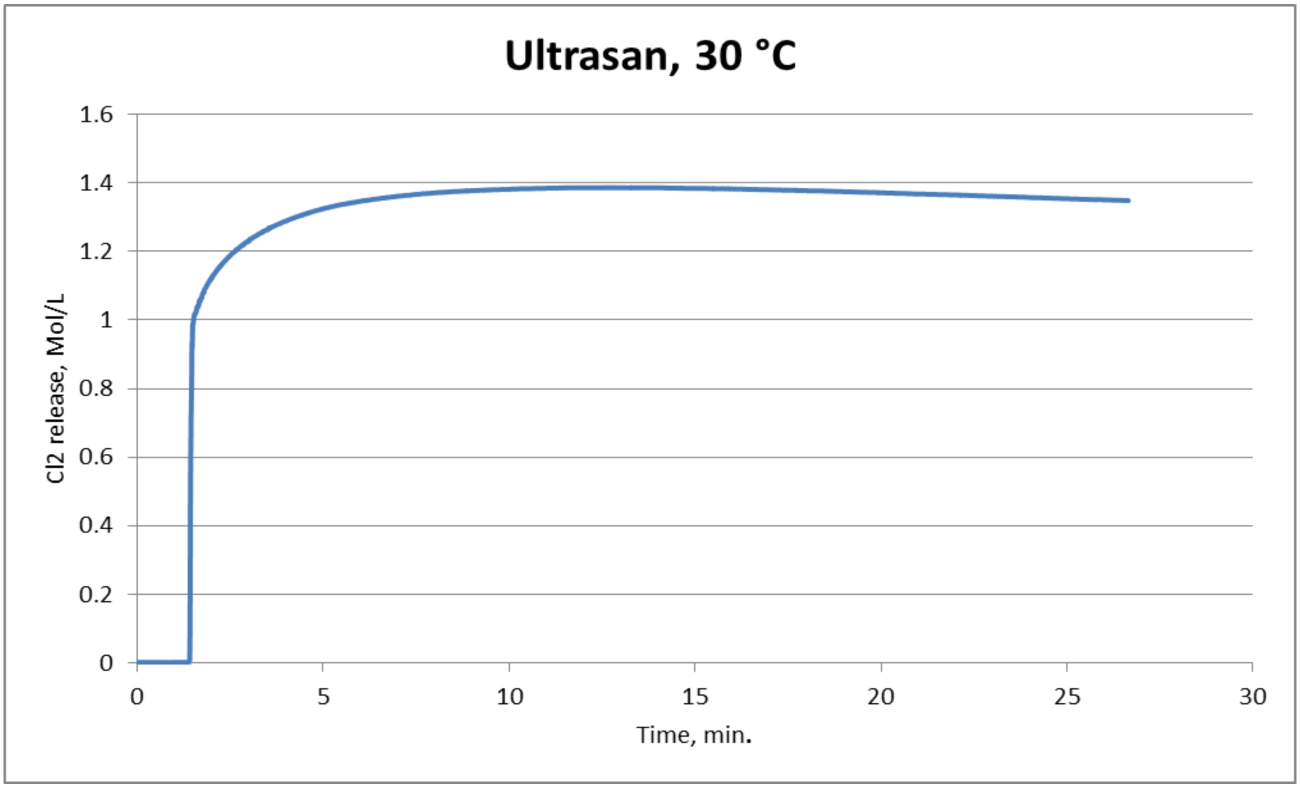


Fig. 32 Chlorine release from Ultra San product reacted with 10% HCl at 30 °C

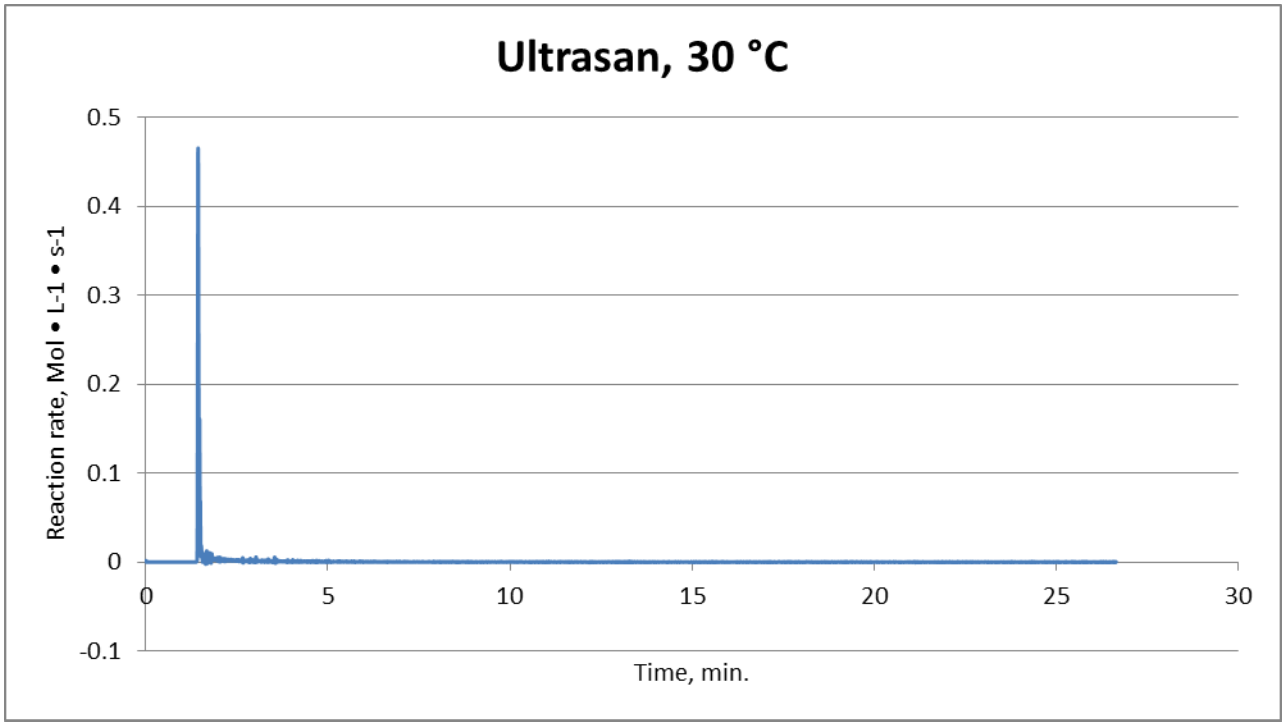


Fig. 33 Instantaneous rate of chlorine release from Ultra San product reacted with 10% HCl at 30 °C

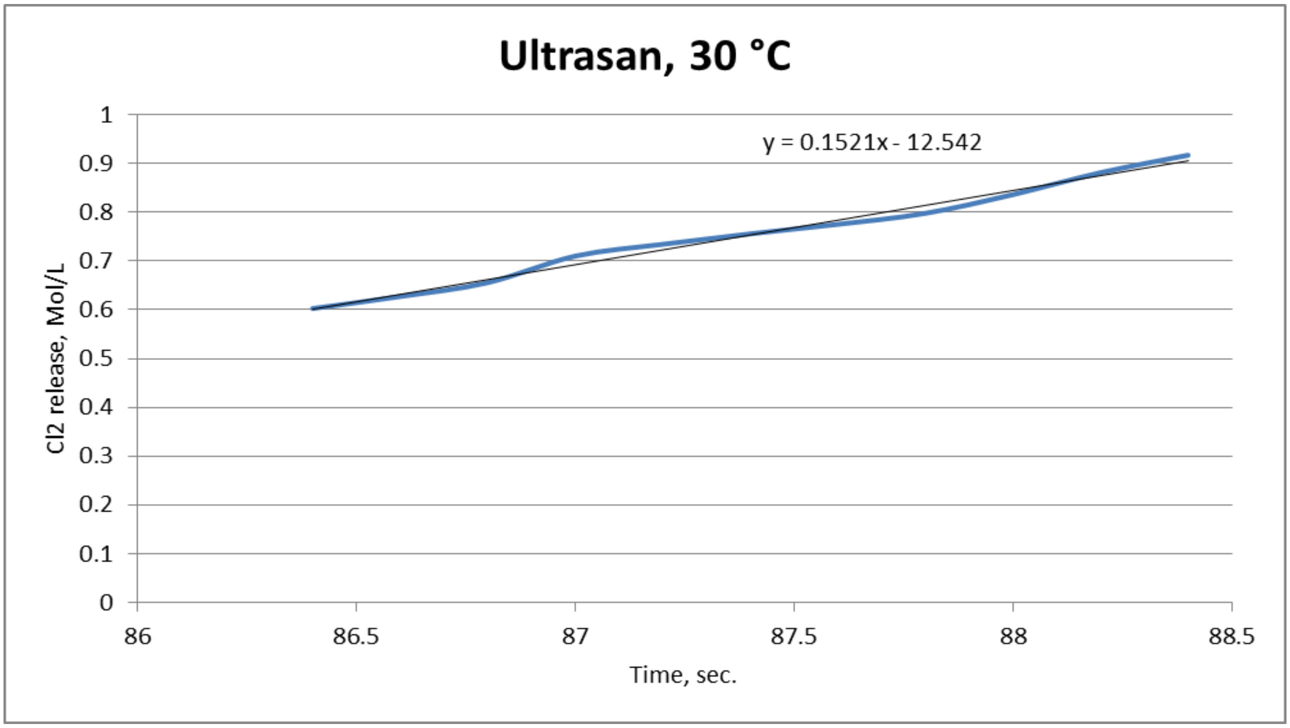


Fig. 34 Chlorine release from Ultra San product reacted with HCl at 30 °C; part used for initial rate calculation.

4.3.1.1. Kinetic study results:

Instantaneous rates of reaction have been registered as thousands rate/time points per experiment; however, one point from each of them with the maximum rate value (Inst. max. rate). This value was used for Arrhenius kinetic parameter calculations.

The initial rate constants were calculated by the least square method using several data points that produced the maximal rate value. Pairs of rate constants for each product will be reported: “Inst. max. rate” and “Initial rate”. Both rates were used to calculate Arrhenius kinetic parameters – Activation energies E_a and Pre-exponential factors A. For more details please refer to the Appendix “Chemical Kinetics Background”.

Table 11. “Inst. max. rates” and “Initial rates” for Ultra San

Ultra San product	Reaction rate, Mol · L^{-1} · s^{-1}		
Rates	15 °C	22 °C	30 °C
Max. rate	0.157	0.17	0.465
Initial rate	0.0914	0.12	0.256

4.3.1.2. Instantaneous maximal rate kinetic parameters:

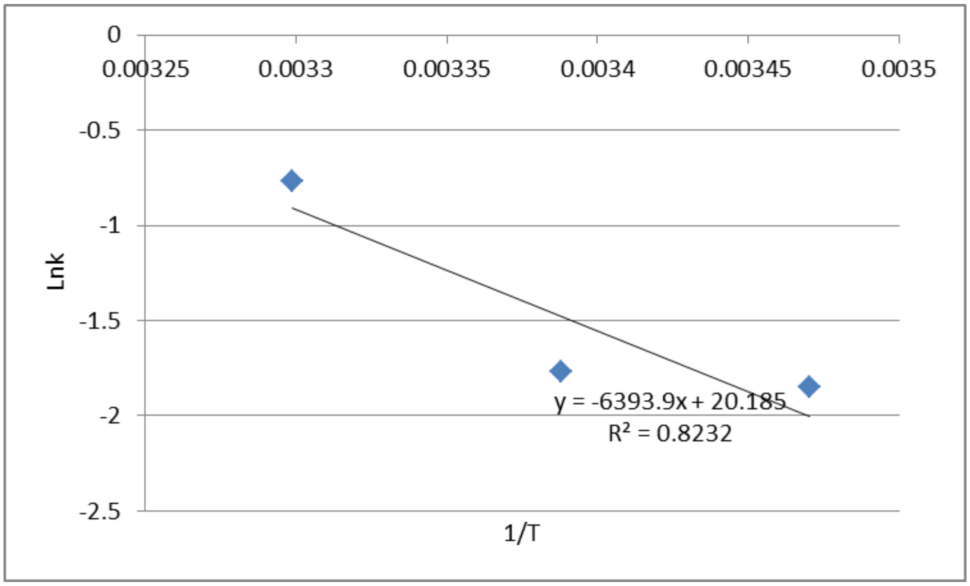


Fig. 35 Arrhenius plot for Inst. max. rate kinetic parameters, Ultra San product

Table 12. Inst. max. rate kinetic parameters, Ultra San product

T	k	1/T	lnk
288.15	0.157	0.00347	-1.85151
295.15	0.17	0.003388	-1.77196
303.15	0.465	0.003299	-0.76572
E_a =	53.16	kJ/Mol	
A=	5.81E+08		

4.3.1.3. Initial rate kinetic parameters:

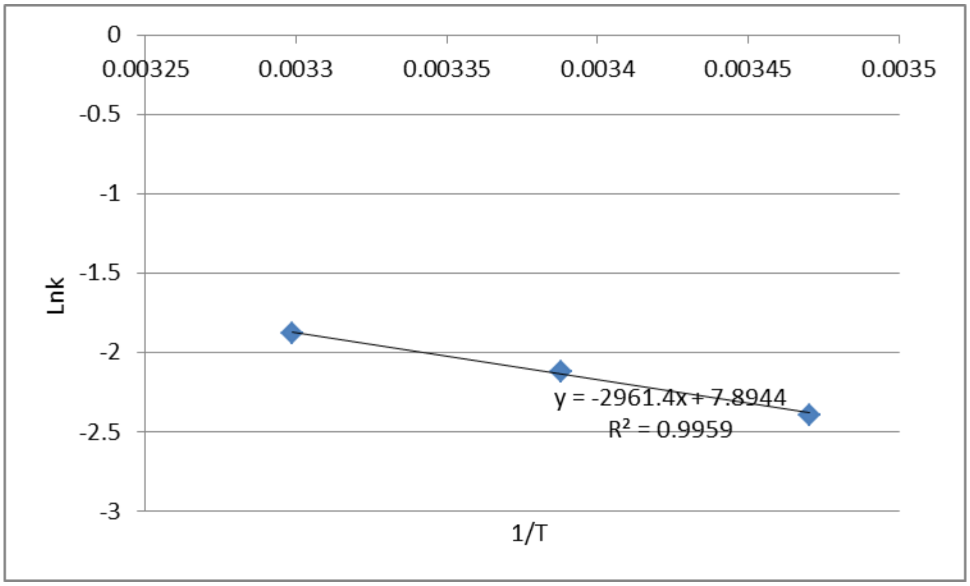


Fig. 36 Arrhenius plot for Initial rate kinetic parameters, Ultra San product

Table 13. Initial rate kinetic parameters, Ultra San product

T	k	1/T	lnk
288.15	0.0914	0.00347	-2.39251
295.15	0.12	0.003388	-2.12026
303.15	0.1521	0.003299	-1.88322
E_a =	24.61775	kJ/Mol	
A=	2.68E+03		

As observed from the results above, the data points on Arrhenius plot for maximums of instantaneous rate has a bigger error ($R^2 = 0.8232$). This is because this method uses apex of the first derivative which could be influenced by different random factors such as chlorine bubbles popping up at random times. The initial rates and initial kinetic parameters were calculated from a large sample size and accordingly have small error and a good linear fit ($R^2 = 0.9959$).

Generally, the reaction of Ultra San with HCl was quite fast, it occurred in a matter of seconds after the acid addition and it should have a strong diffusion and mixing dependence.

4.3.2. Javel-12, by SANY:

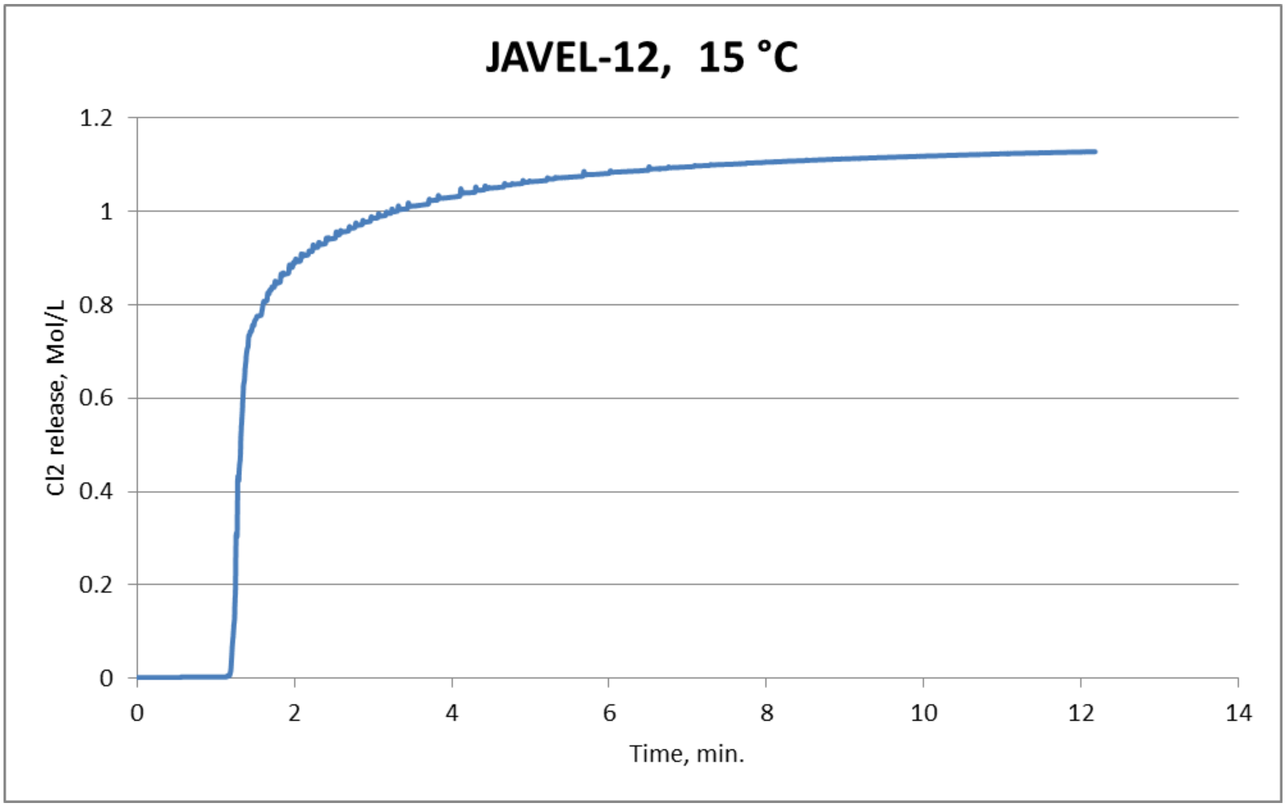


Fig. 37 Chlorine release from Javel 12 product reacted with 10% HCl at 15 °C

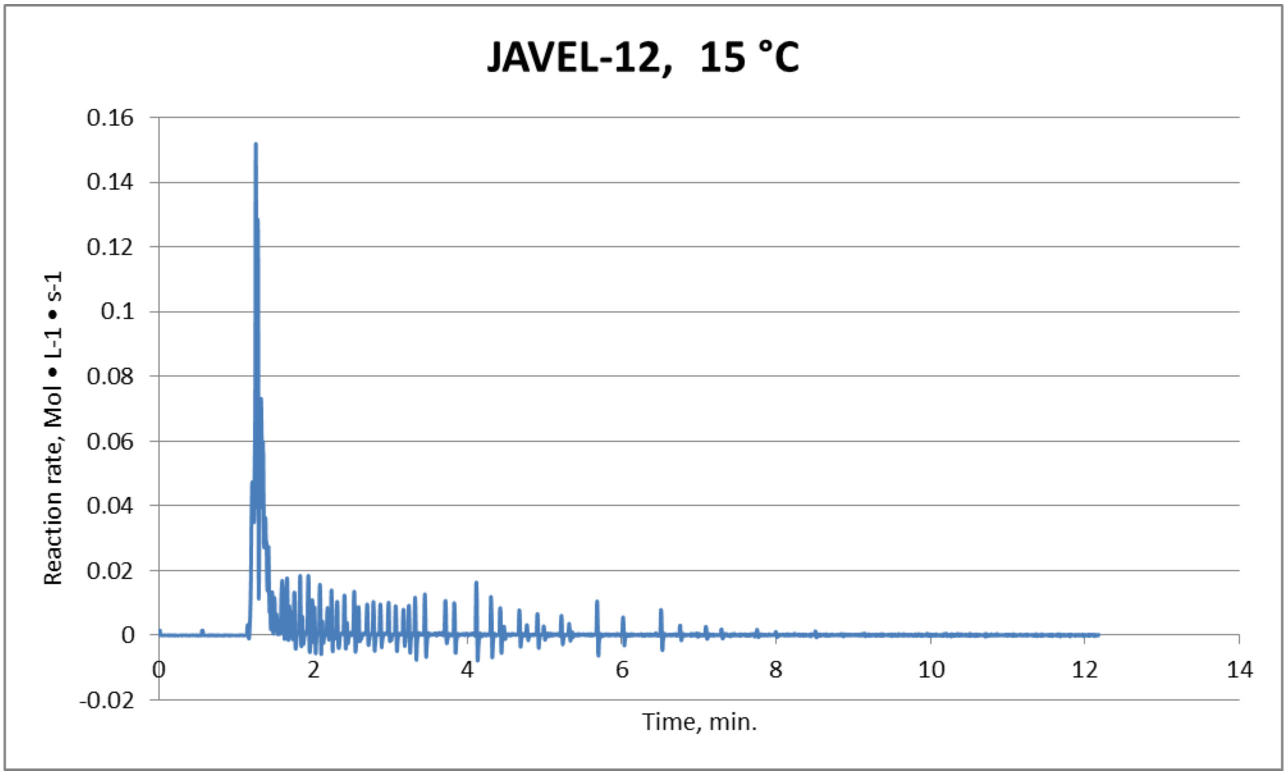


Fig. 38 Instantaneous rate of chlorine release from Javel-12 product reacted with 10% HCl at 15 °C

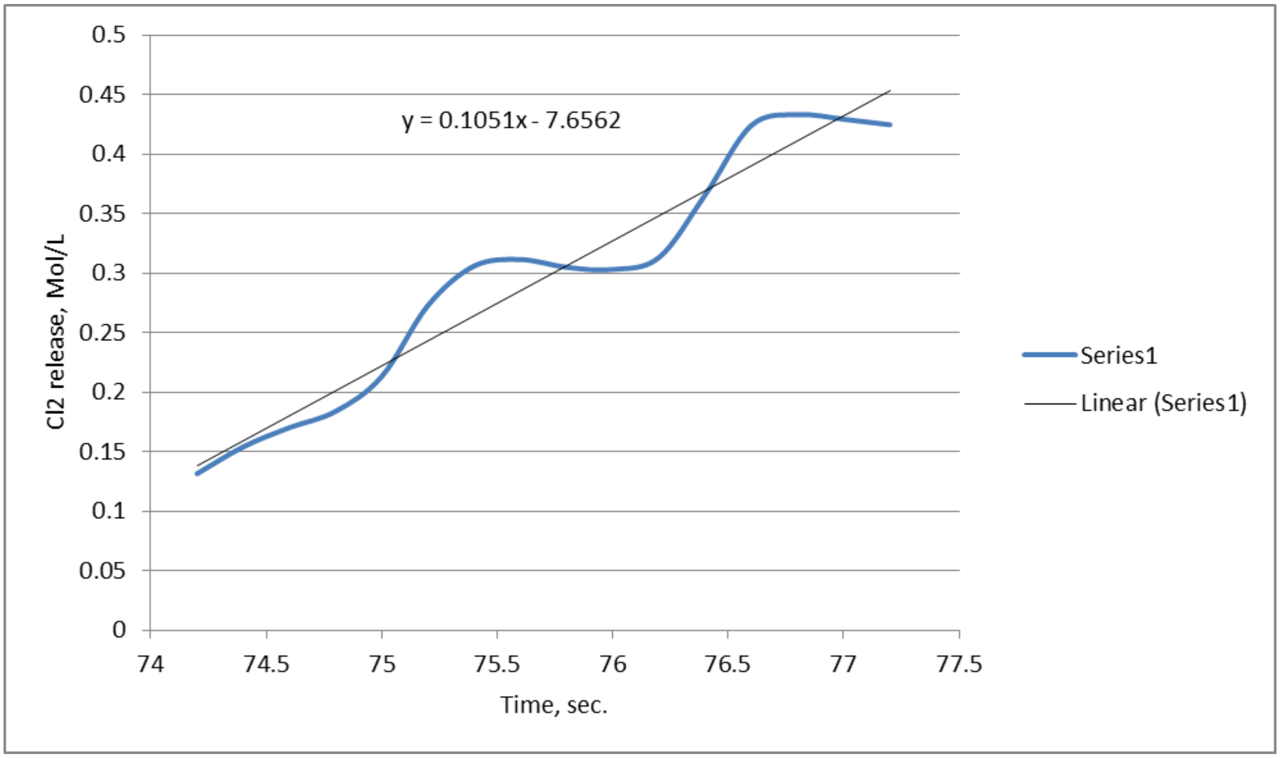


Fig. 39 Chlorine release from Javel-12 product reacted with 10% HCl at 15 °C; part used for initial rate calculation.

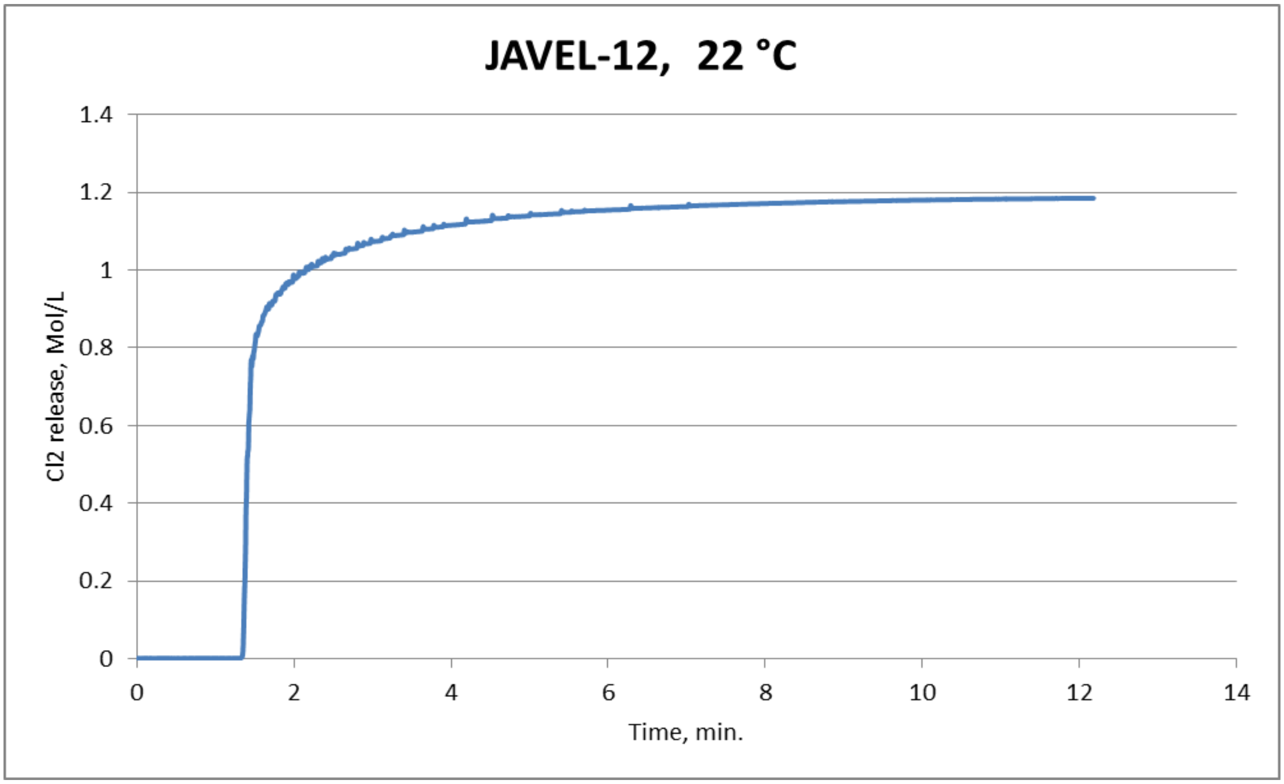


Fig. 40 Chlorine release from Javel-12 product reacted with 10% HCl at 22 °C

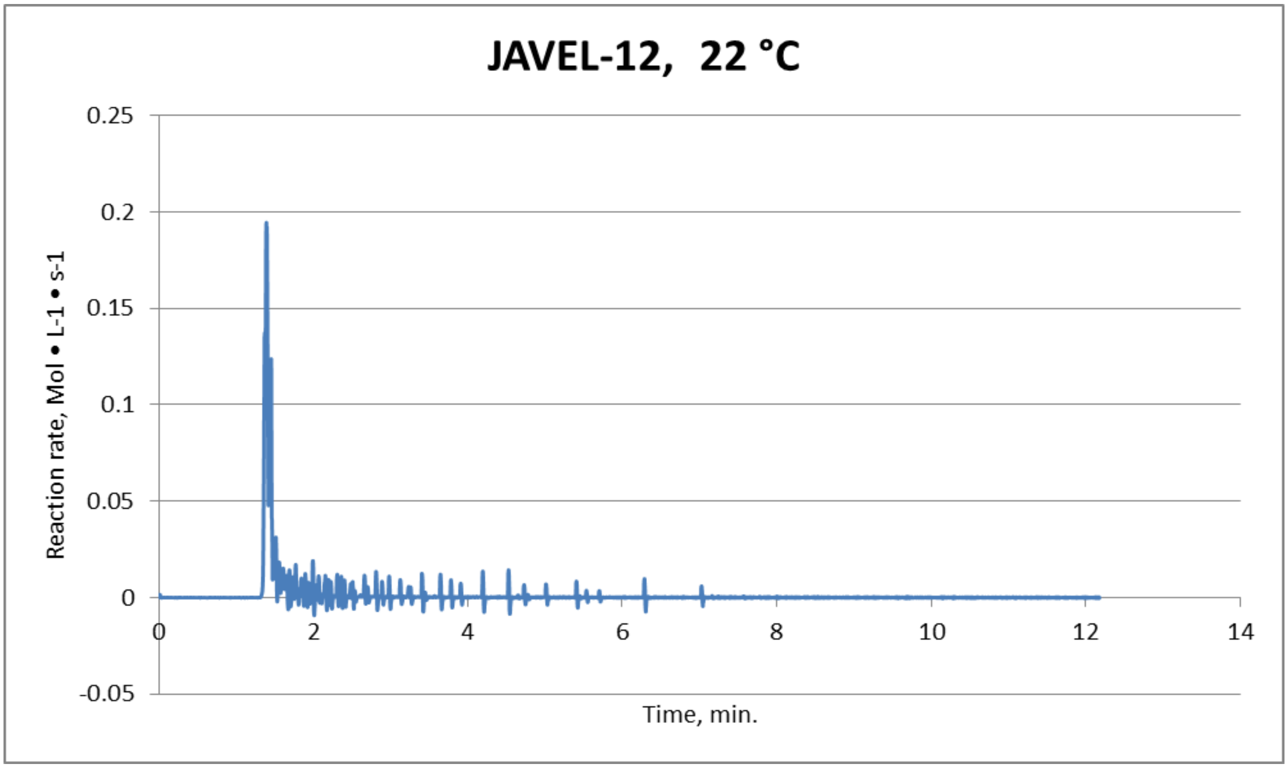


Fig. 41 Instantaneous rate of chlorine release from Javel-12 product reacted with 10% HCl at 22 °C

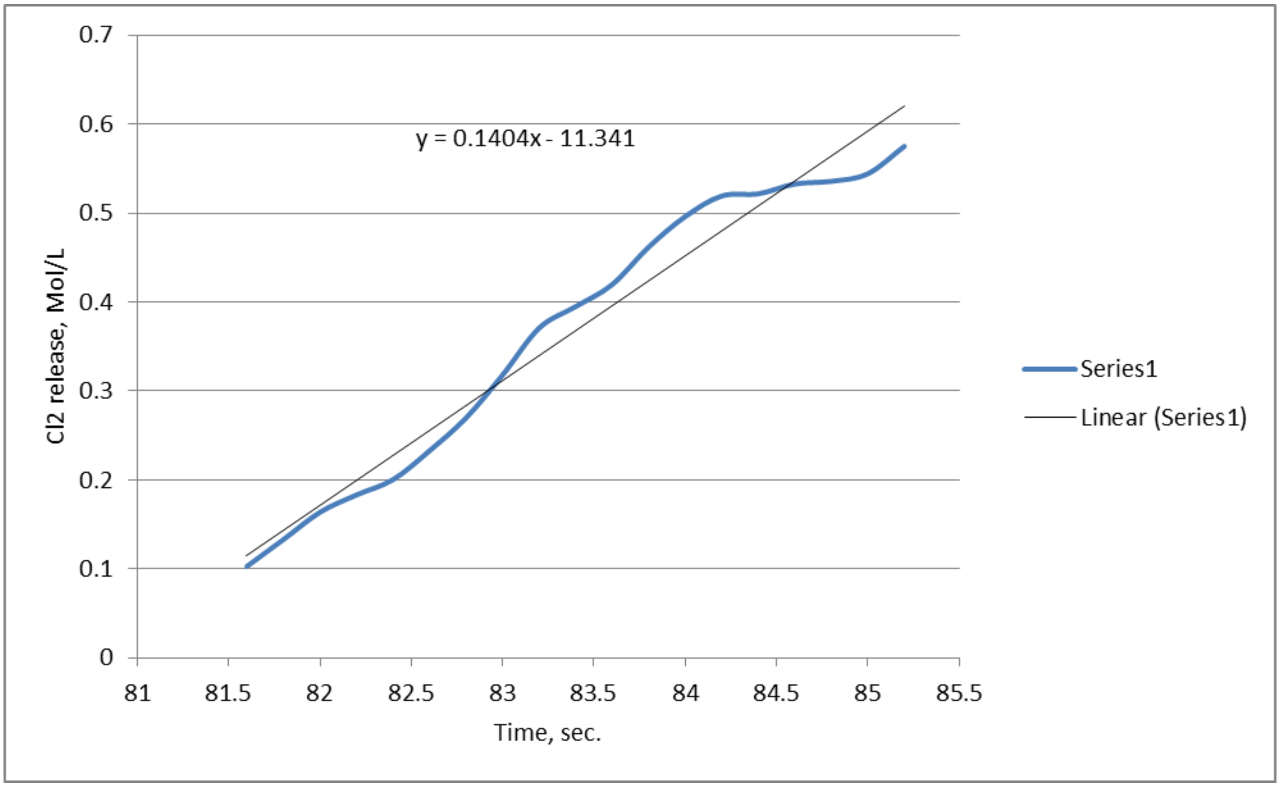


Fig. 42 Chlorine release from Javel-12 product reacted with 10% HCl at 22 °C; part used for initial rate calculation.

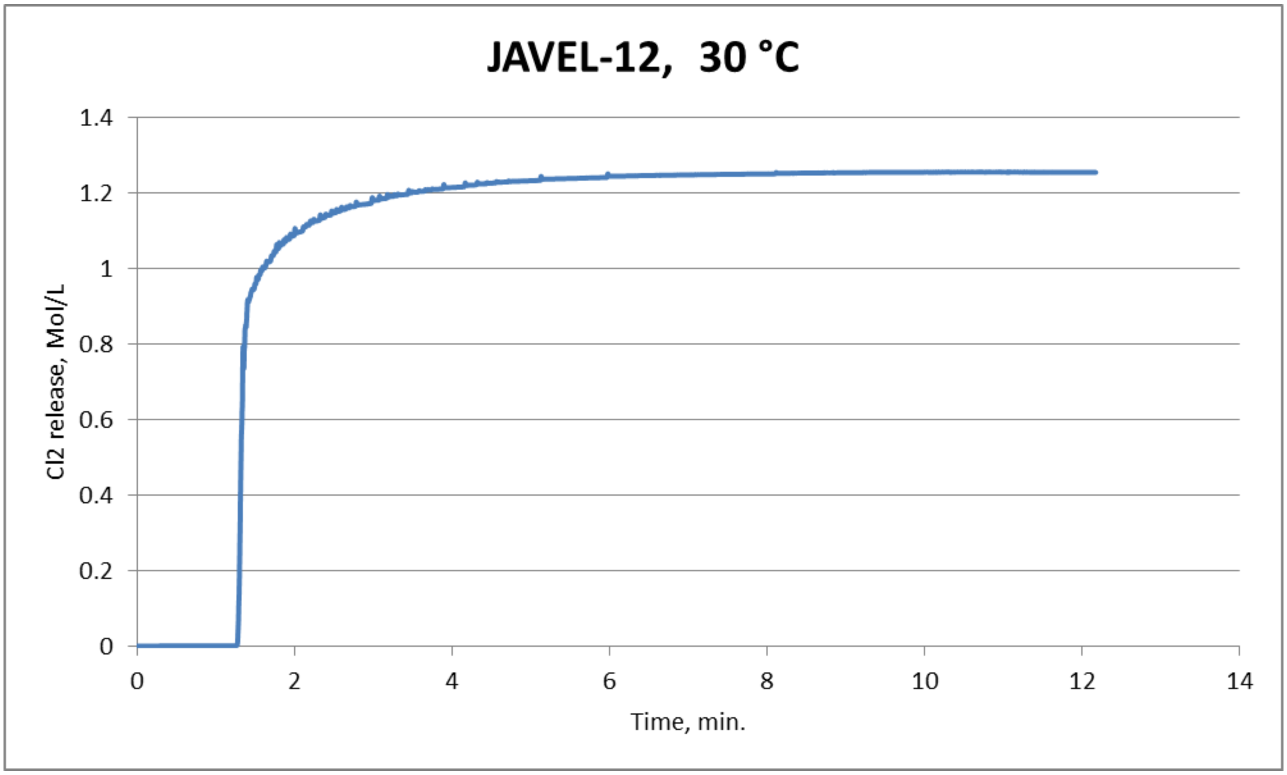


Fig. 43 Chlorine release from Javel-12 product reacted with 10% HCl at 30 °C

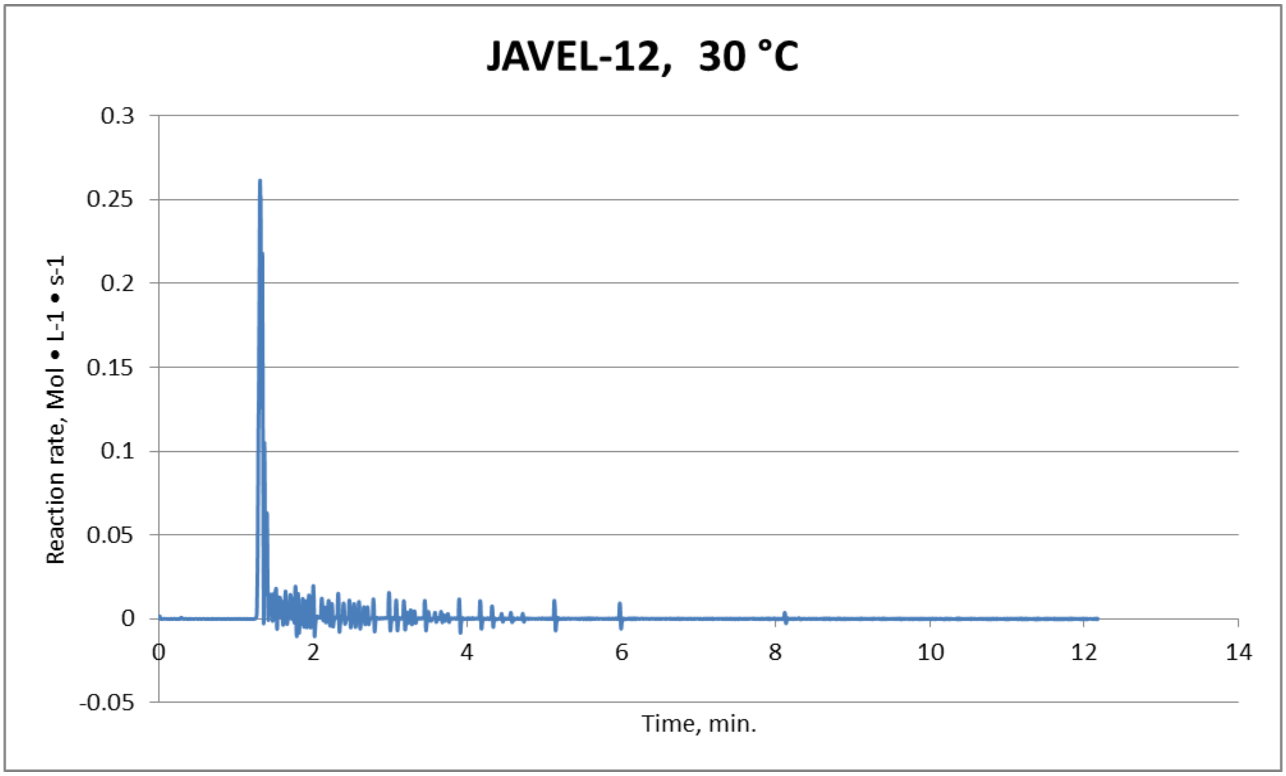


Fig. 44 Instantaneous rate of chlorine release from Javel-12 product reacted with 10% HCl at 30 °C

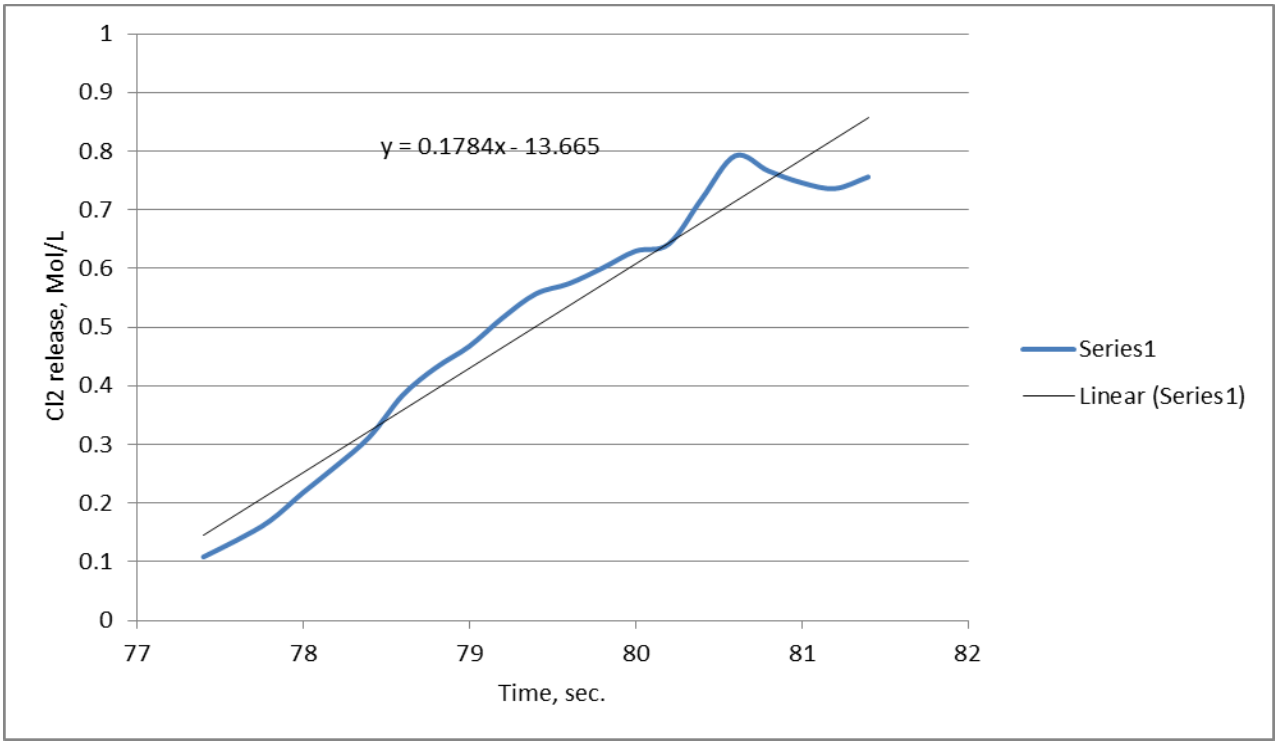


Fig. 45 Chlorine release from Javel-12 product reacted with 10% HCl at 30 °C; part used for initial rate calculation.

4.3.2.1. *Kinetic study results:*

Table 14. “Inst. max. rates” and “Initial rates” for Javel-12 product

Javel-12	Reaction rate, Mol · L^{-1} · s^{-1}		
Rates	15 °C	22 °C	30 °C
Max rate	0.152	0.192	0.261
initial rate	0.1051	0.14	0.1784

4.3.2.2. *Instantaneous maximal rate kinetic parameters:*

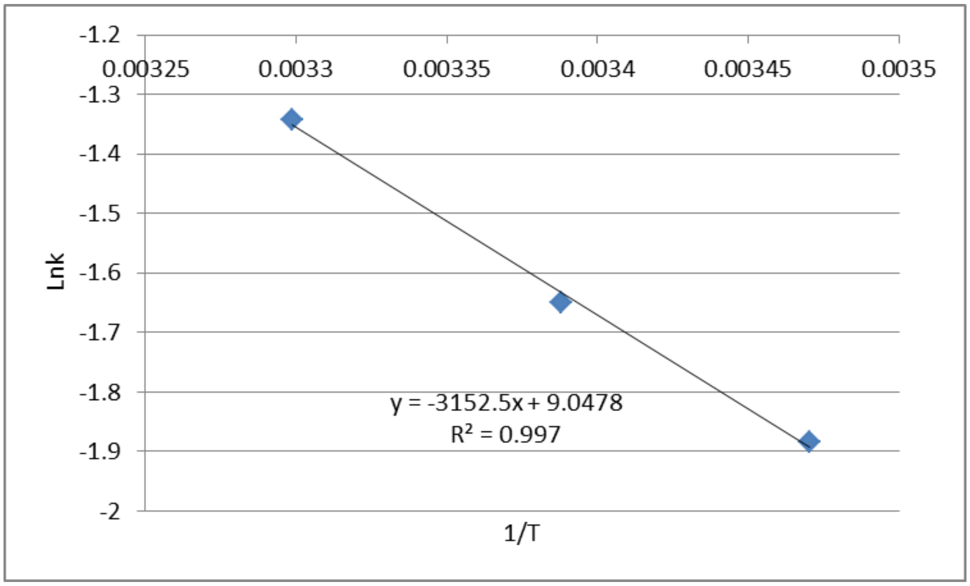


Fig. 46 Arrhenius plot for Instantaneous maximal rate kinetic parameters, Javel-12 product

Table 15. Instantaneous maximal rate kinetic parameters, Javel-12 product

T	k	1/T	lnk
288.15	0.152	0.00347	-1.88387
295.15	0.192	0.003388	-1.65026
303.15	0.261	0.003299	-1.34323
E_a =	26.20989	kJ/Mol	
A=	8.50E+03		

4.3.2.3. *Initial kinetic parameters:*

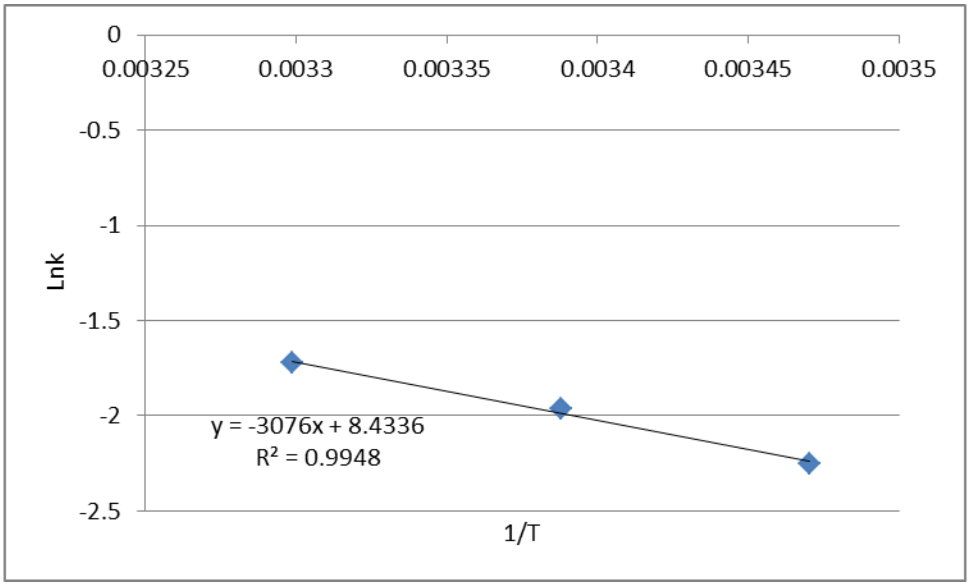


Fig. 47 Arrhenius plot for Initialrate kinetic parameters, Javel-12 product

Table 16. Initial rate kinetic parameters, Javel-12 product

T	k	1/T	lnk
288.15	0.1051	0.00347	-2.25284
295.15	0.14	0.003388	-1.96611
303.15	0.1784	0.003299	-1.72373
E_a =	25.57386	kJ/Mol	
A=	8.50E+03		

4.3.3. Liquid Plumr, by Clorox

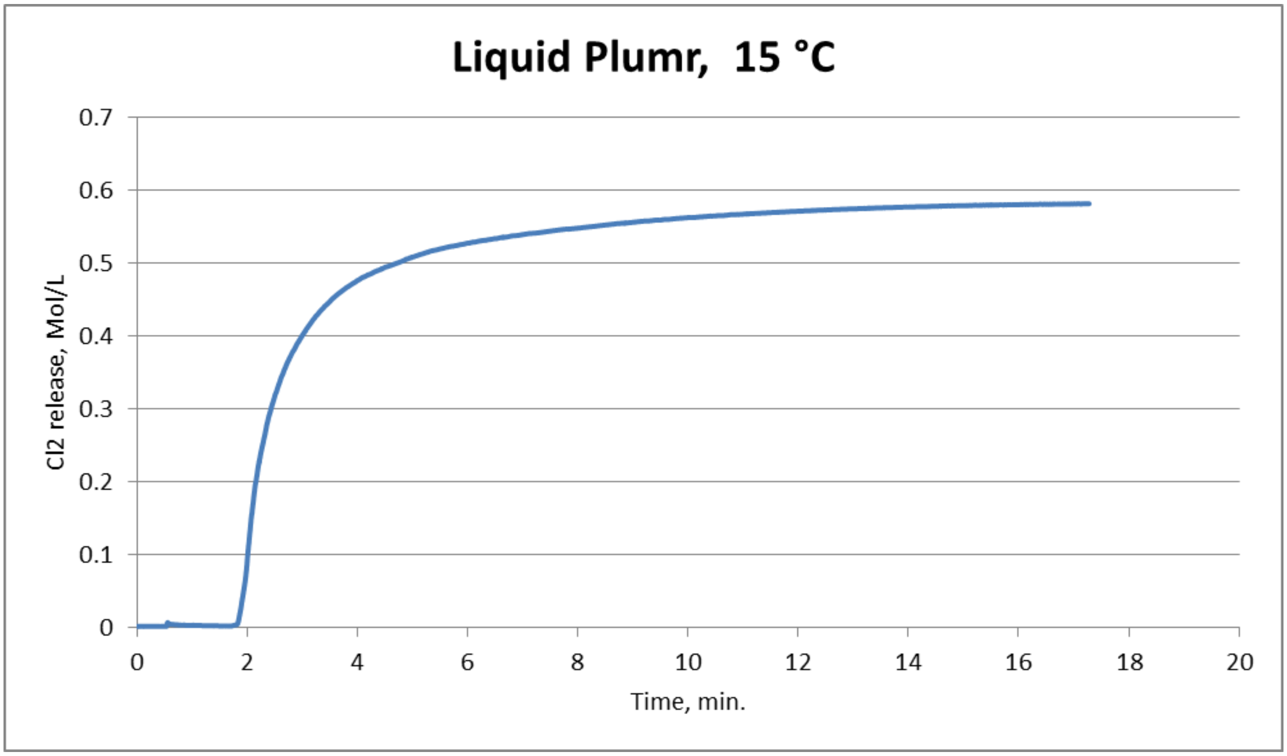


Fig. 48 Chlorine release from Liquid Plumr product reacted with 10% HCl at 15 °C

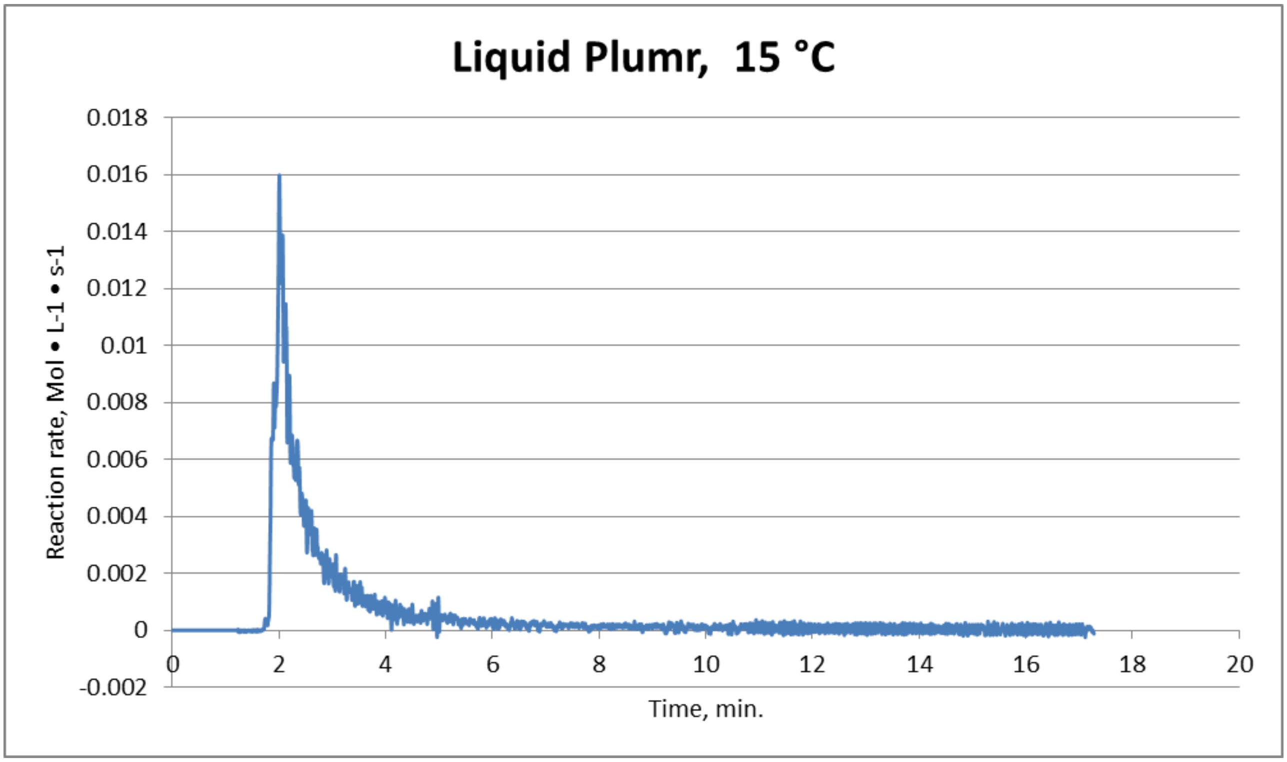


Fig. 49 Instantaneous rate of chlorine release from Liquid Plumr product reacted with 10% HCl at 15 °C

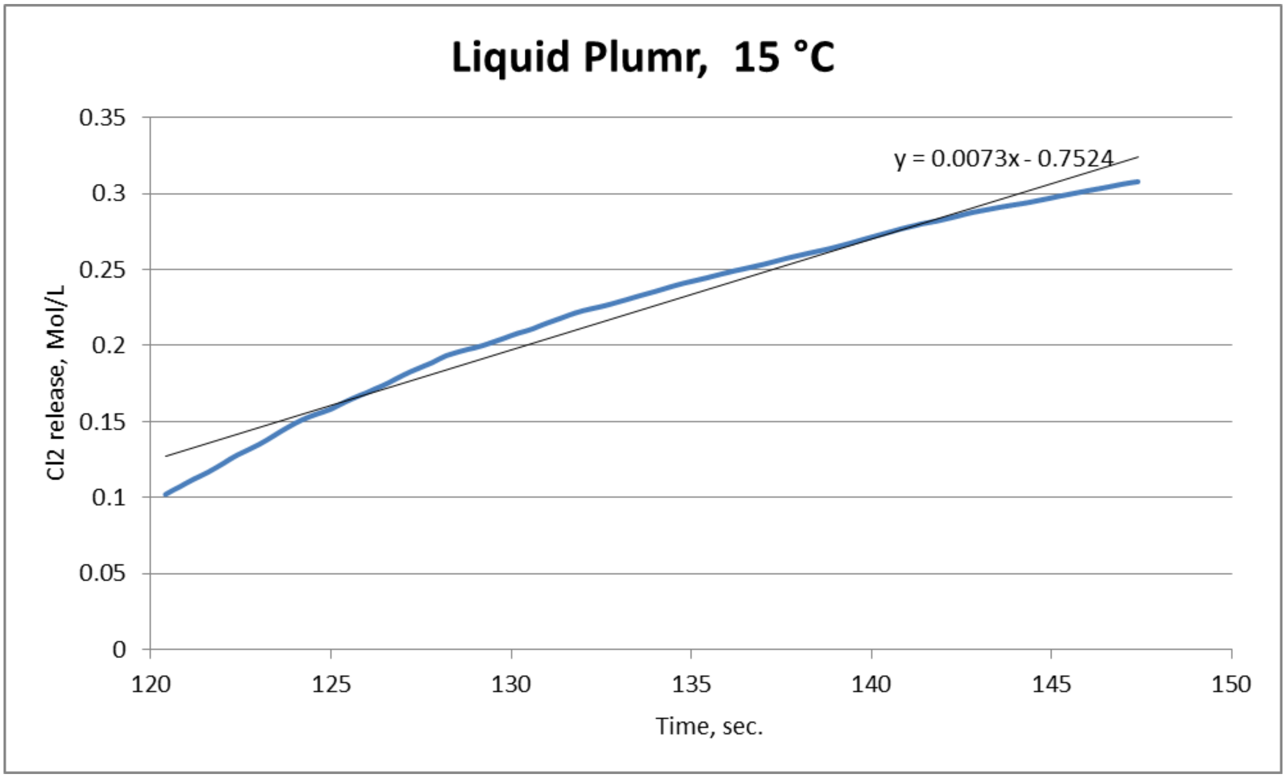


Fig. 50 Chlorine release from Liquid Plumr product reacted with 10% HCl at 15 °C; part used for initial rate calculation.

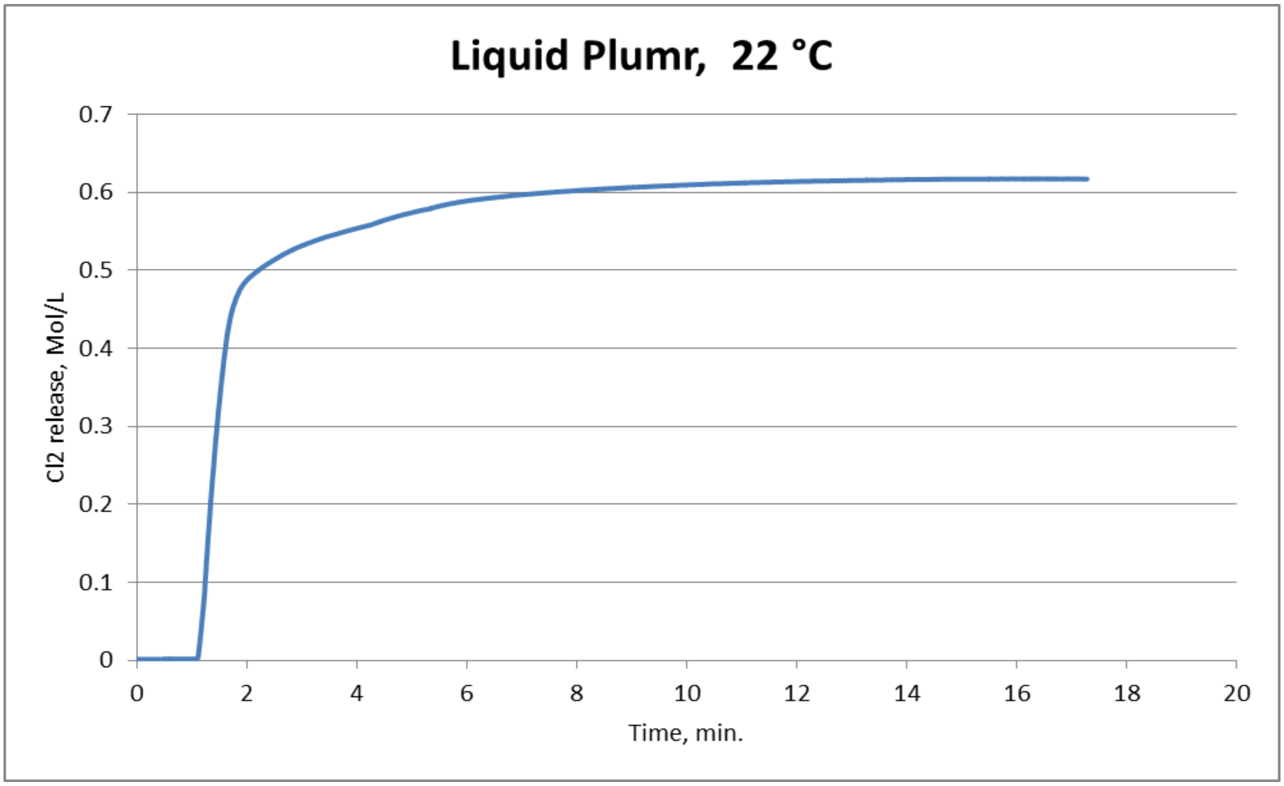


Fig. 51 Chlorine release from Liquid Plumr product reacted with 10% HCl at 22 °C

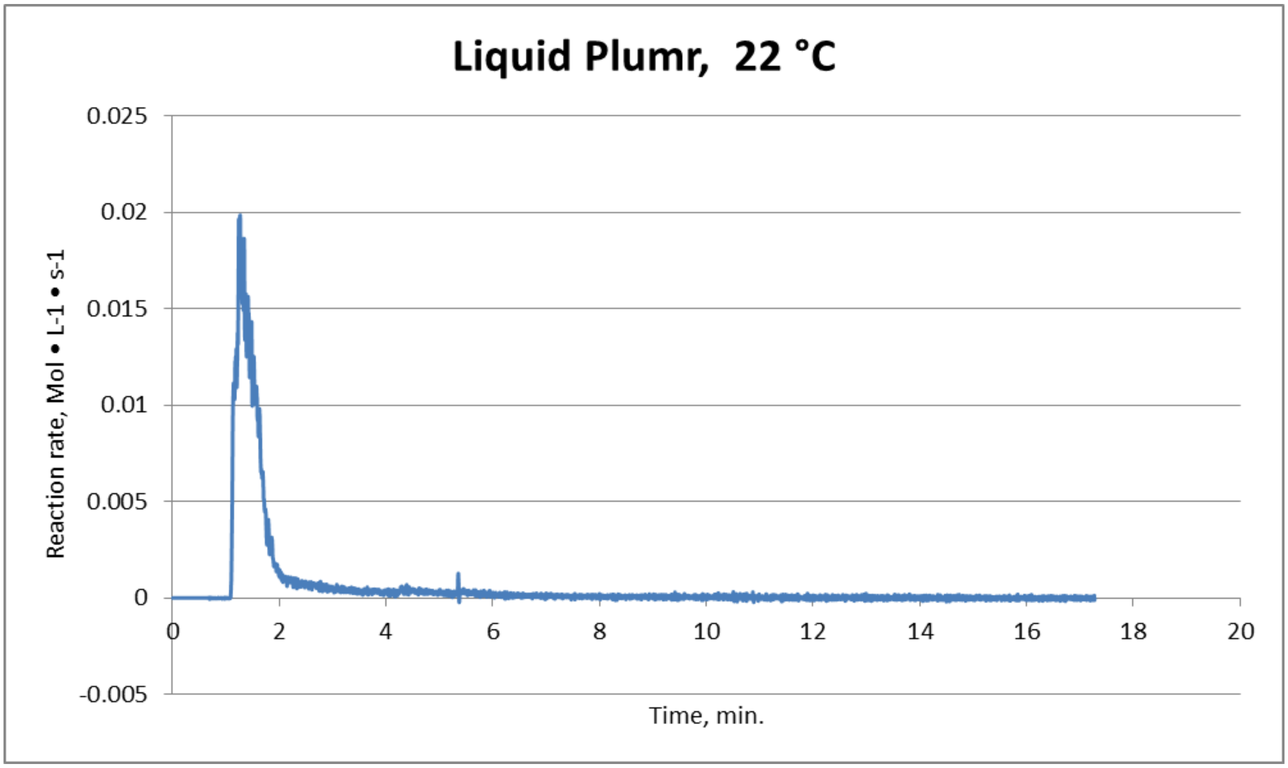


Fig. 52 Instantaneous rate of chlorine release from Liquid Plumr product reacted with 10% HCl at 22 °C

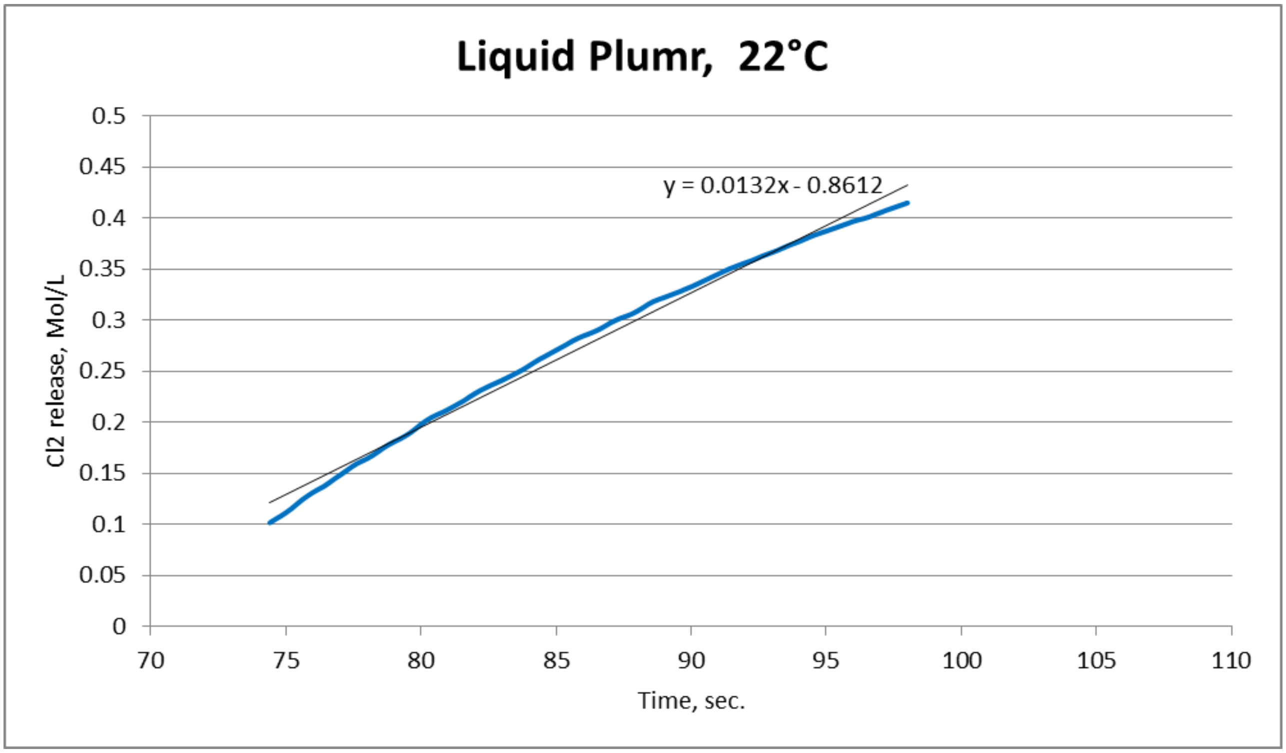


Fig. 53 Chlorine release from Liquid Plumr product reacted with 10% HCl at 22 °C; part used for initial rate calculation.

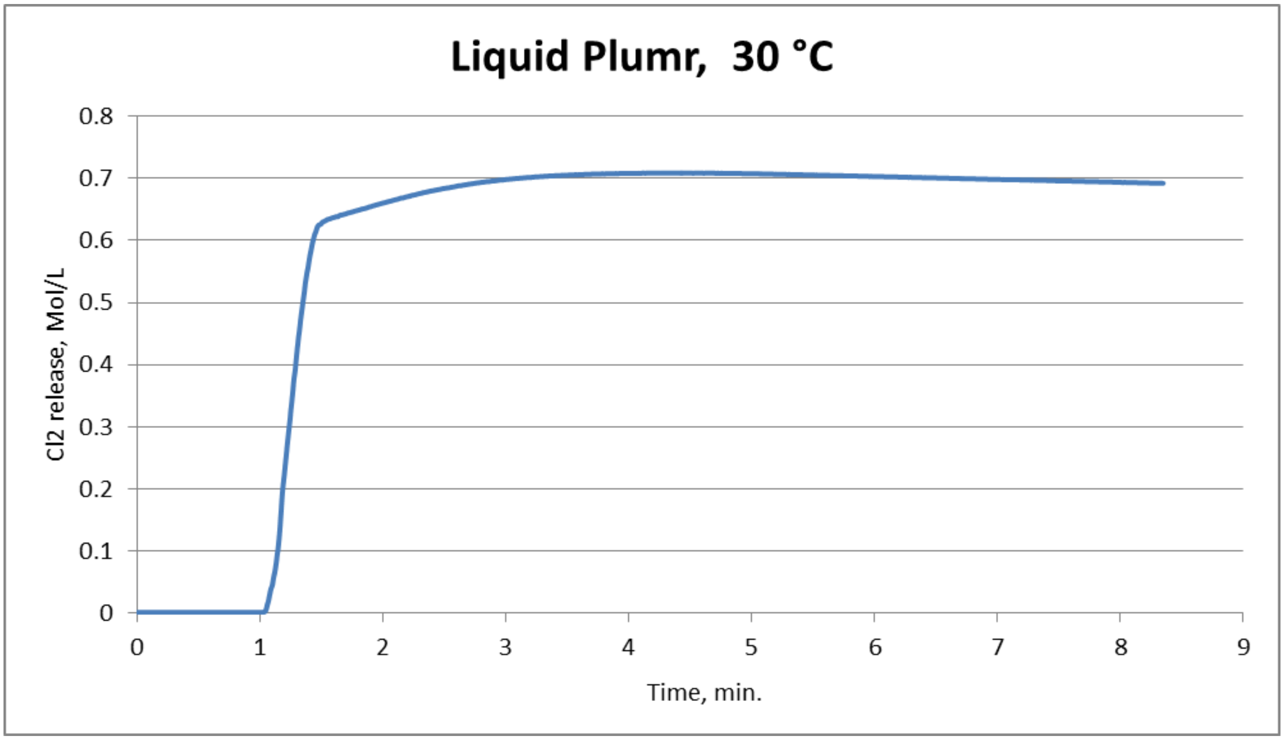


Fig. 54 Chlorine release from Liquid Plumr product reacted with 10% HCl at 30 °C

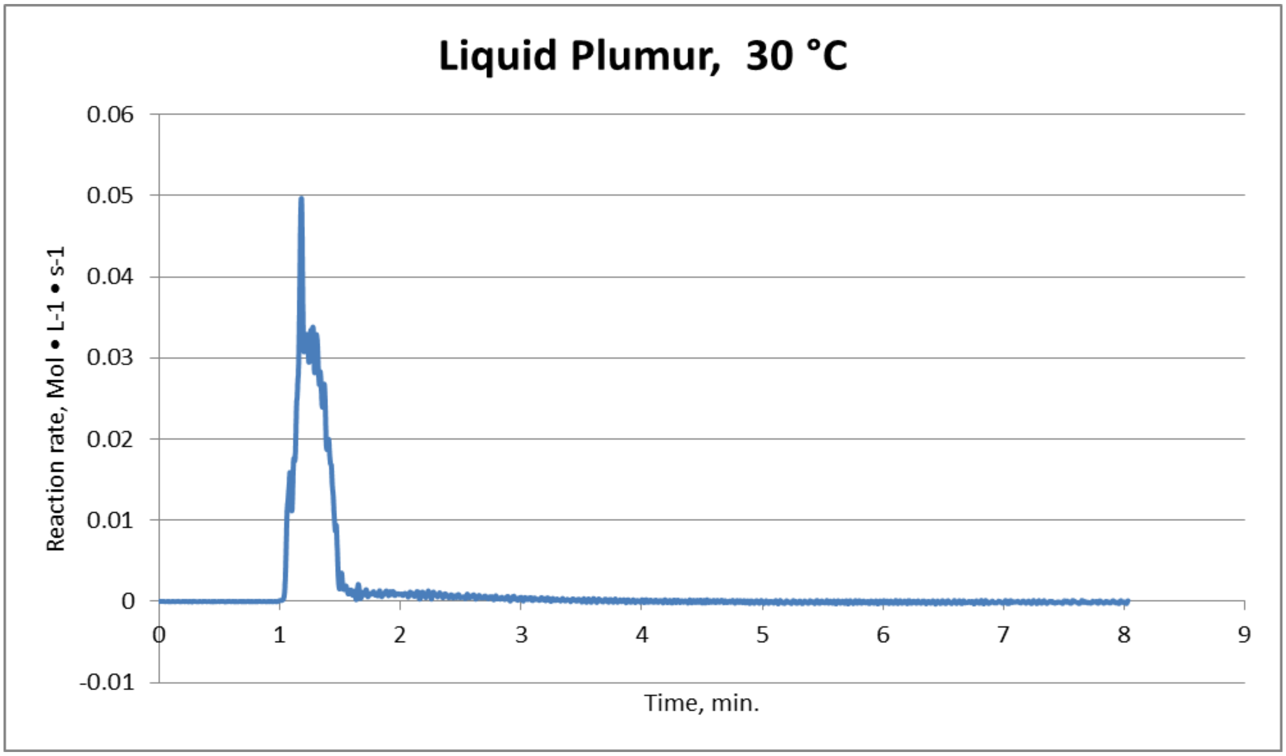


Fig. 55 Instantaneous rate of chlorine release from Liquid Plumr product reacted with 10% HCl at 30 °C

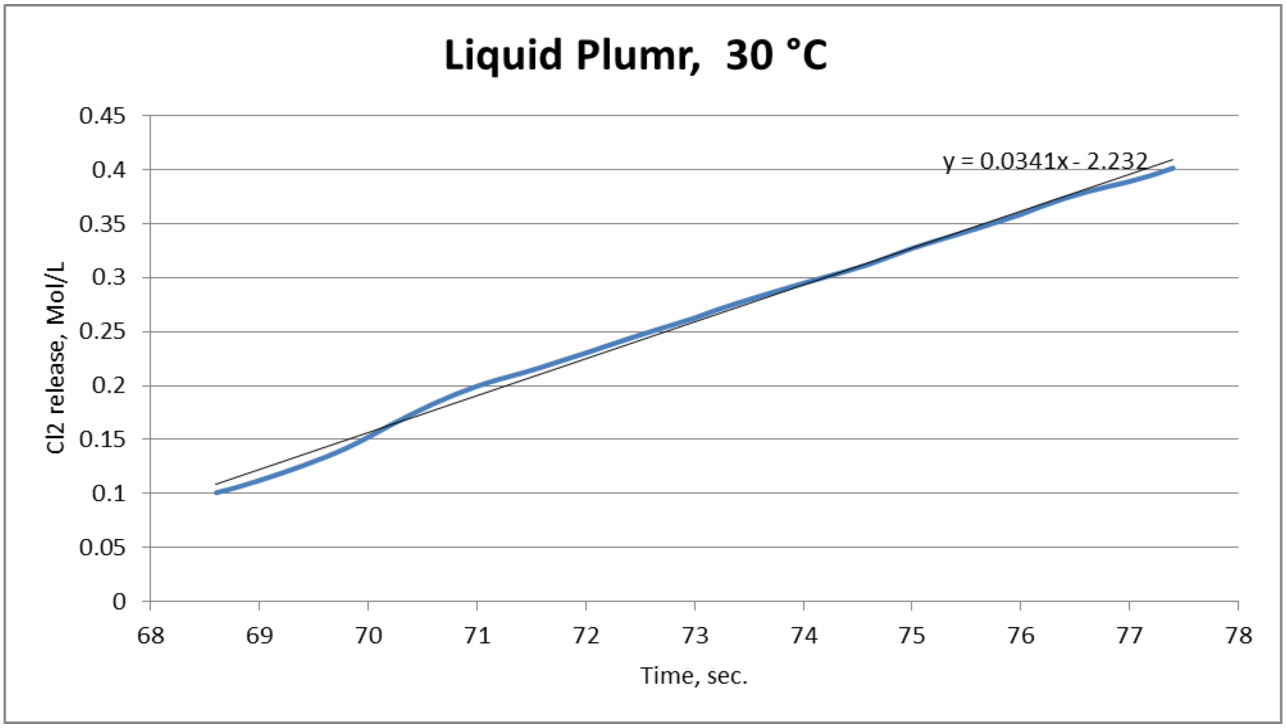


Fig. 56 Chlorine release from Liquid Plumr product reacted with 10% HCl at 30 °C; part used for initial rate calculation.

4.3.3.1. *Kinetic study results:*

Table 17. "Inst. max. rates" and "Initial rates" for Liquid Plumr product

Liquid Plumr	Reaction rate, Mol · L^{-1} · s^{-1}		
Rates	15 °C	22 °C	30 °C
Max rate	0.0158	0.0196	0.0496
initial rate	0.0073	0.0132	0.0341

4.3.3.2. *Instantaneous maximal rate kinetic parameters:*

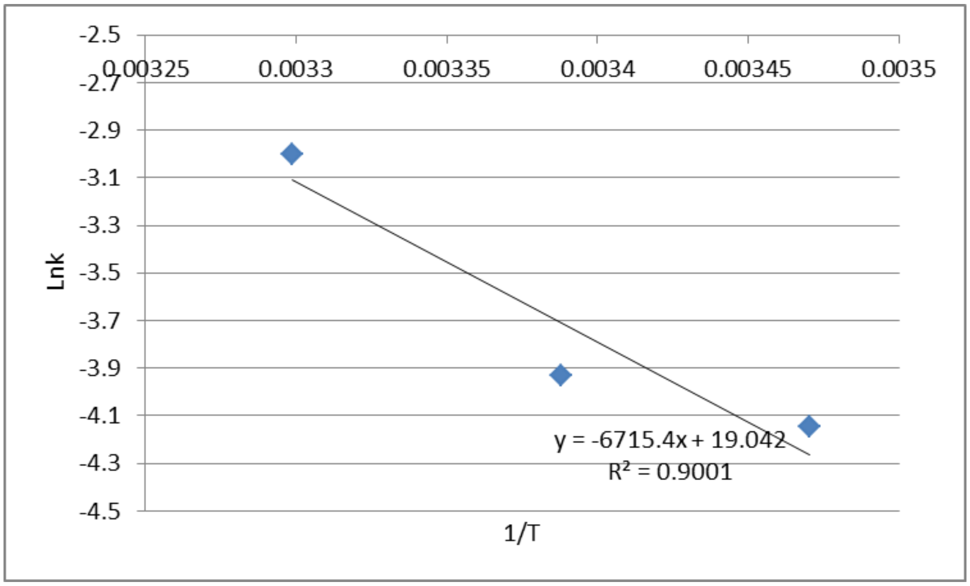


Fig. 57 Arrhenius plot for Instantaneous maximal kinetic parameters, Liquid Plumr product

Table 18. Instantaneous maximal kinetic parameters, Liquid Plumr product

T	k	1/T	lnk
288.15	0.0158	0.00347	-4.14775
295.15	0.0196	0.003388	-3.93223
303.15	0.0496	0.003299	-3.00376
E_a =	55.82851	kJ/Mol	
A=	1.86E+08		

4.3.3.3. *Initial kinetic parameters:*

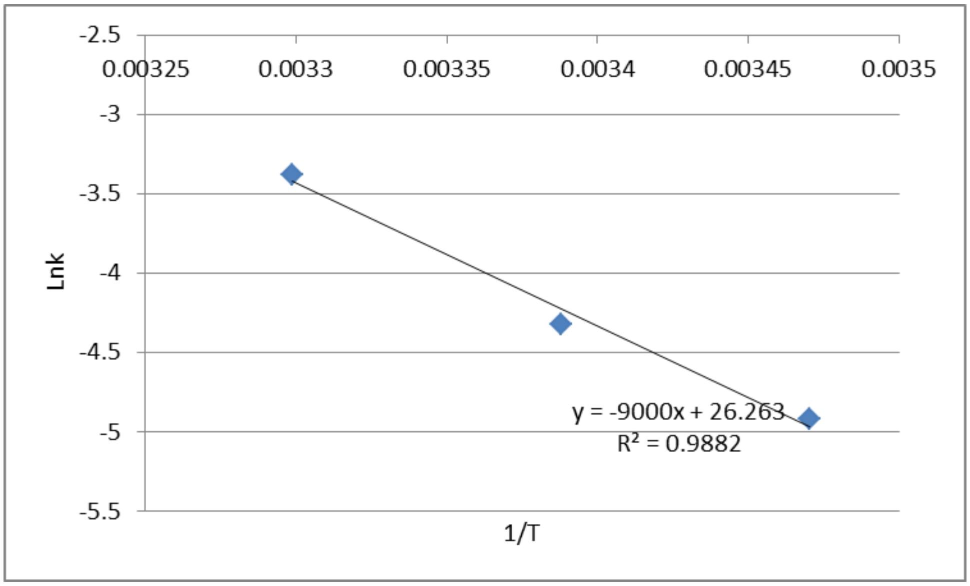


Fig. 58 Arrhenius plot for Initial kinetic parameters, Liquid Plumr product

Table 19. Initial kinetic parameters, Liquid Plumr product

T	k	1/T	lnk
288.15	0.0073	0.00347	-4.91988
295.15	0.0132	0.003388	-4.32754
303.15	0.0341	0.003299	-3.37846
E_a =	74.826	kJ/Mol	
A=	2.55E+11		

4.3.4. Stabilized chlorinating pucks by hth (Trichloro-S-Triazinetrione)

Stabilized chlorinating pucks were ground into a fine powder and this powder was used in the experiments to facilitate the reaction and the chlorine release.

Reactions of Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione) with water were very slow. During the experiment, a small fraction of the product reacted with water and therefore there was a small change of concentration of it in the water. In addition, the reaction mixture had a certain amount of solid product that kept water solution saturated and accordingly at a constant concentration. As a result, the reaction rate remained constant during the period of the experiment (1 hr). In case of a constant reaction rate initial and instantaneous reaction rates are equal, and due to this, reported only one rate value by experiment.

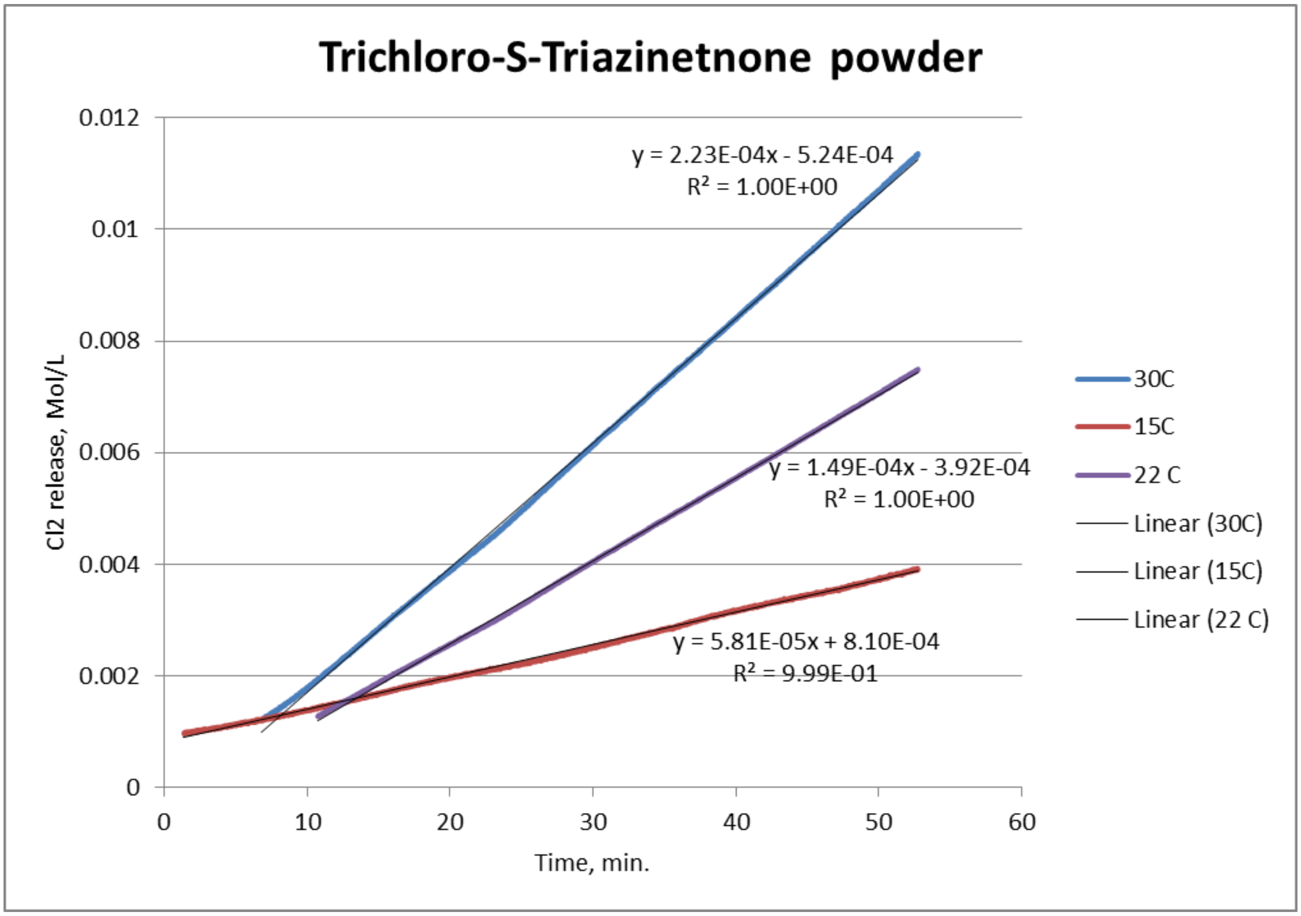


Fig. 59 Chlorine release from Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione) reacted with water at 30 °C (blue), 22 °C (purple) and 15 °C (red).

Table 20. Chlorine release rates from Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione) reacted with water

Temperature	Reaction rate, Mol · L^{-1} · s^{-1}
15	9.68E-07
22	2.48E-06
30	3.72E-06

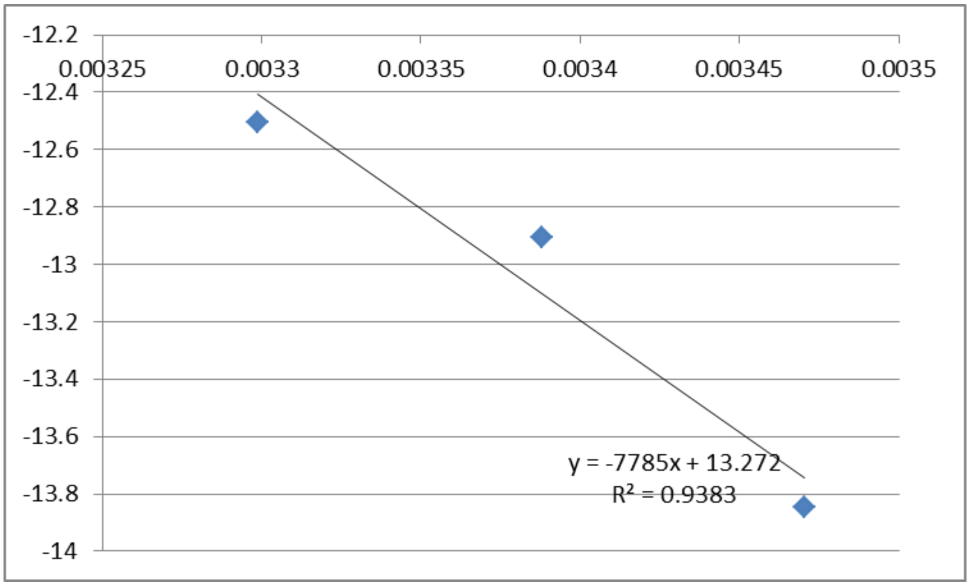


Fig. 60 Arrhenius plot for kinetic parameters, Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione) reacted with water.

Table 21. Kinetic parameters, Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione) reacted with water

T	k	1/T	lnk
288.15	9.68E-07	0.00347	-13.8477
295.15	2.48E-06	0.003388	-12.9059
303.15	3.72E-06	0.003299	-12.5027
E_a =	64.72449	kJ/Mol	
A=	5.81E+05		

4.3.5. Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate)

Reactions of Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate) with water were very slow, 3 to 5 times slower than reactions of Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione). Again, the reaction rates remained constant during the period of the experiment (1 hr) and accordingly, reported only one rate value by experiment.

It was noted not a strong dependence of reaction rates on temperature; the Arrhenius parameters may not be very useful in this case, however, they were calculated:

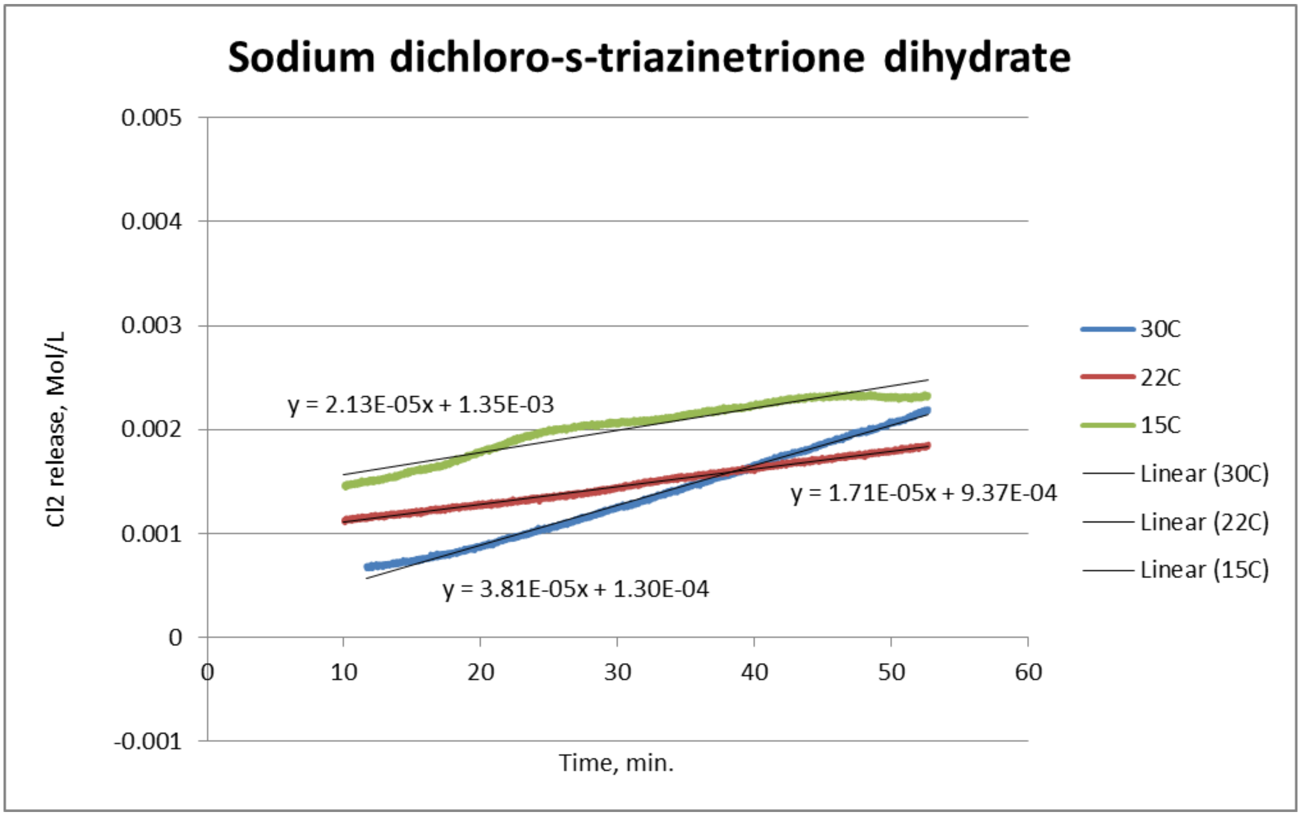


Fig. 61 Chlorine release from Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate) reacted with water at 30 °C (blue), 22 °C (red) and 15 °C (green).

Table 22. Chlorine release rates from Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate) reacted with water

Temperature	Reaction rate, mol · L^{-1} · s^{-1}
15	3.55E-07
22	2.85E-07
30	6.35E-07

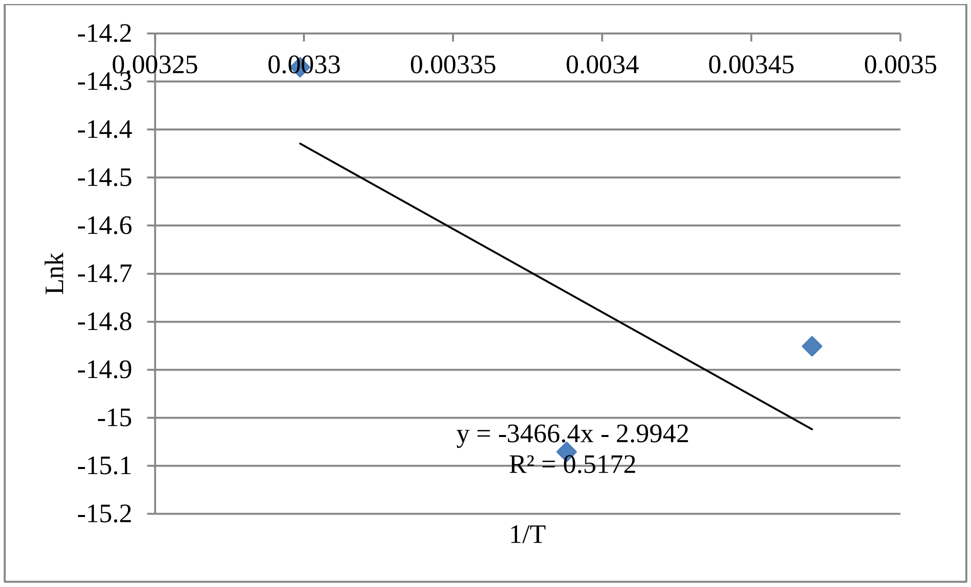


Fig. 62 Arrhenius plot for kinetic parameters, Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate) reacted with water.

Table 23. Kinetic parameters, Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate) reacted with water.

T	k	1/T	lnk
288.15	3.55E-07	0.00347	-14.8511
295.15	2.85E-07	0.003388	-15.0708
303.15	6.35E-07	0.003299	-14.2696
E_a =	28.81965	kJ/Mol	
A=	1.99E+01		

4.3.6. Super Shock, by hth (Calcium Hypochlorite)

Super Shock, by hth (Calcium Hypochlorite) while mixed with water, produced a lot of heat but no chlorine release was detected. Calcium hypochlorite had small chlorine concentration, but this small chlorine concentration in the reactor filled with calcium hypochlorite decreased on addition of water.

It was difficult to estimate the rate of chlorine release in the reaction between Super Shock, by hth (Calcium Hypochlorite) and water at any temperature. Please see Fig. 63.

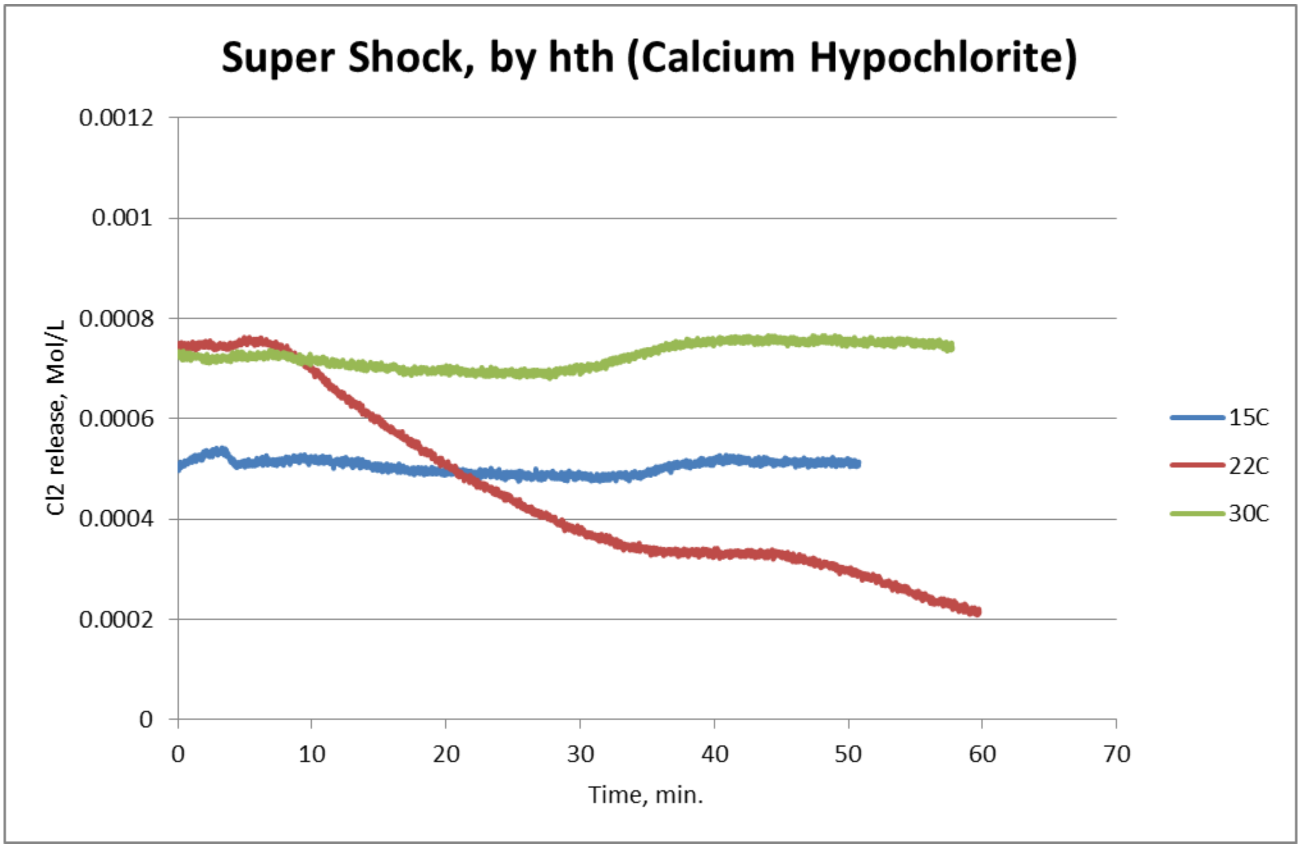


Fig. 63 Chlorine release from Super Shock, by hth (Calcium Hypochlorite) reacted with water at 30 °C (green), 22 °C (red) and 15 °C (blue).

4.3.7. Conclusion for Task 3:

The reaction rates of liquid products were very high, Ultra San and Javel-12 had similar rates of chlorine release, despite the 2% concentration difference. The reactions started instantly and the majority of chlorine release happened within a few seconds after the acid addition.

The chlorine release rate at 30 °C could reach 0.5 $mol \cdot L^{-1} \cdot s^{-1}$, this means that from one liter of a product will be released about 12 liters of chlorine during the first second of the reaction. This will create an extremely toxic chlorine cloud.

Liquid Plumr had about 10 times slower chlorine release rate (0.05 $mol \cdot L^{-1} \cdot s^{-1}$as maximum). This can be explained by a lower sodium hypochlorite concentration and a very high viscosity. In the case of an accident, 1 liter of Liquid Plumr would release about 1.2 L of chlorine during the first second and this is still dangerous.

Energies of activation, E_a, for Ultra San and Javel-12 are similar, nearly equal to 25 kJ/mol.

The energy of activation for liquid Plumr is more than two times higher (74 kJ/Mol), this fact can be explained by the complicated composition of this product – it has a high viscosity that decreases (in 10 times) the rate of reaction however, the viscosity could decrease with a temperature increase. As a result, the reaction rate becomes more dependent on the temperature.

The solid products studied released chlorine at a very low rate:

- 2.48E-06 $mol \cdot L^{-1} \cdot s^{-1}$ (22 °C) for Trichloro-S-Triazinetrione;
- 2.85E-07 $mol \cdot L^{-1} \cdot s^{-1}$ (22 °C) for Sodium dichloro-s-triazinetrione dihydrate;
- Negligible to zero for calcium hypochlorite.

Wetting of tested solid products poses no immediate danger to human health. However, in a closed or not ventilated setup, Trichloro-S-Triazinetrione and Sodium dichloro-s-triazinetrione dihydrate can create potentially dangerous chlorine concentrations: one kilogram of wet Trichloro-S-Triazinetrione can release 21 mL of chlorine per hour and wet Sodium dichloro-s-triazinetrione dihydrate can release 2.5 mL of chlorine per kg per hour. Calcium hypochlorite appeared to be the least reactive, and no chlorine release has been detected. However, it is a highly toxic and an active compound that contains a lot of active chlorine. It can violently react with compounds other than water, so it may not be considered as 100% "safe".

4.4. Task 4 — Assessing the Effect of Mixing on the Rate of Reaction

The objective of Task 4 was assessing the effect of mixing speed on the rate of reaction. Mixing speed and the apparent reaction rate are intrinsically related, the faster the reactants are brought together, the higher the rate of the reaction.

Task 4 looked at the kinetic parameters of reactions of 3 liquid products with 10% HCl and 3 solid products with water at 3 temperatures (15, 22, and 30°C) and at 4 different mixing speeds (0, 50, 100 and 300 rpm). The hypochlorite products tested in Task 4 are the same as used in Tasks 2 and 3.

In experiments under Task 4, hydrochloric acid was added to a product as a laminar flow on top of the product to avoid extensive initial mixing. As a result, acid and product were mixed by a magnetic stirrer at a precise speed; in case of speed = 0 the acid and a product initially formed two layers and they reacted on the interface, gradually mixing together.

TASK 4 results:

Units if not stated otherwise are:

- Chlorine release rate: $Mol \times L^{-1} \times s^{-1}$
- Chlorine release: $Mol \times L^{-1}$
- E_a: $kJ \times Mol^{-1}$
- A : s^{-1}
- T: K
- Mixing speed: *rpm = 1/60 Hz*

4.4.1. Product: JAVEL-12 by SANY:

Javel-12, 15 °C

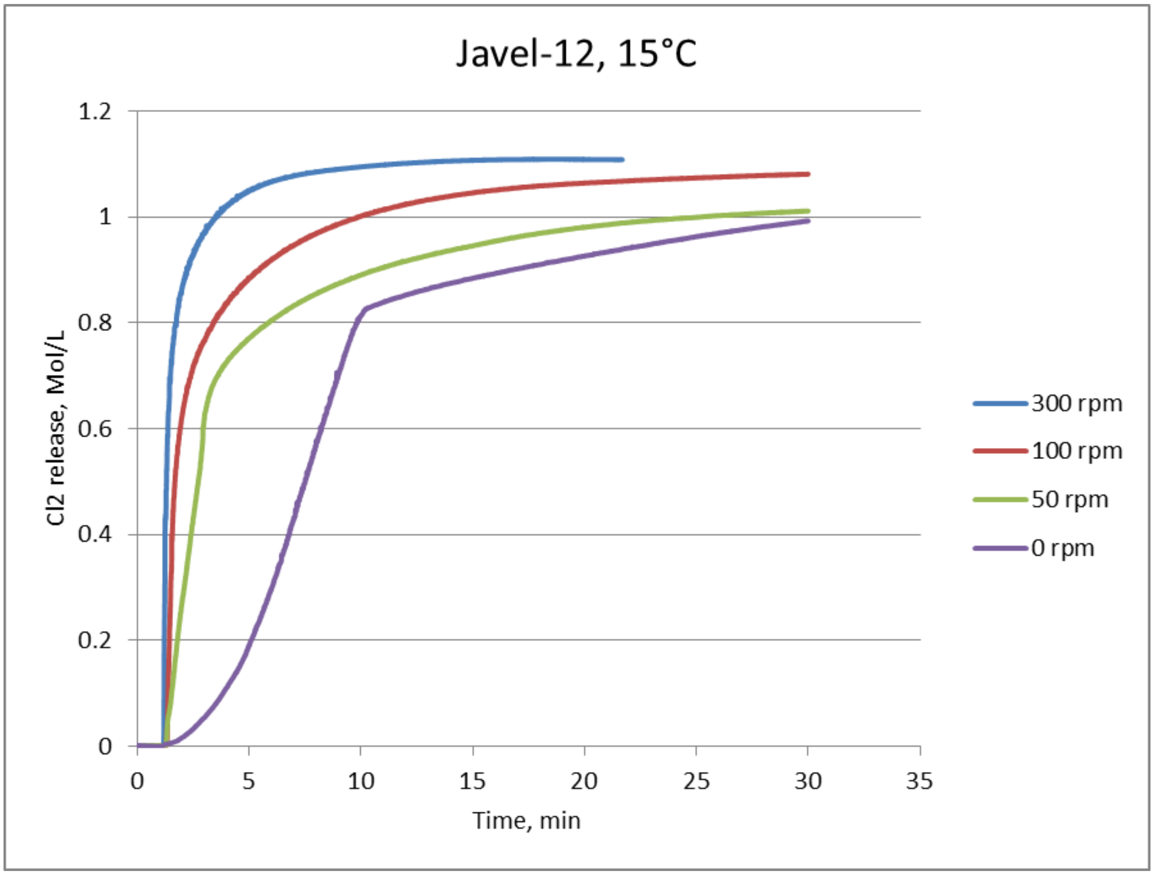


Fig. 64 Chlorine release from Javel-12 product reacted with HCl at 15 °C and different mixing speeds

Table 24. Initial and instantaneous (maximal point) rates of chlorine release from Javel-12 product at 15 °C:

Initial

Speed	Rate
0	8.77E-04
50	6.18E-03
100	2.75E-02
300	1.05E-01

Inst. max. rate

Speed	Rate
0	1.80E-02
50	2.58E-02
100	6.65E-02
300	1.81E-01

In the experiments with different mixing speeds extremely high dependence of reaction rates on the mixing speed were observed; the shape of chlorine release curves also was affected at low mixing speeds.

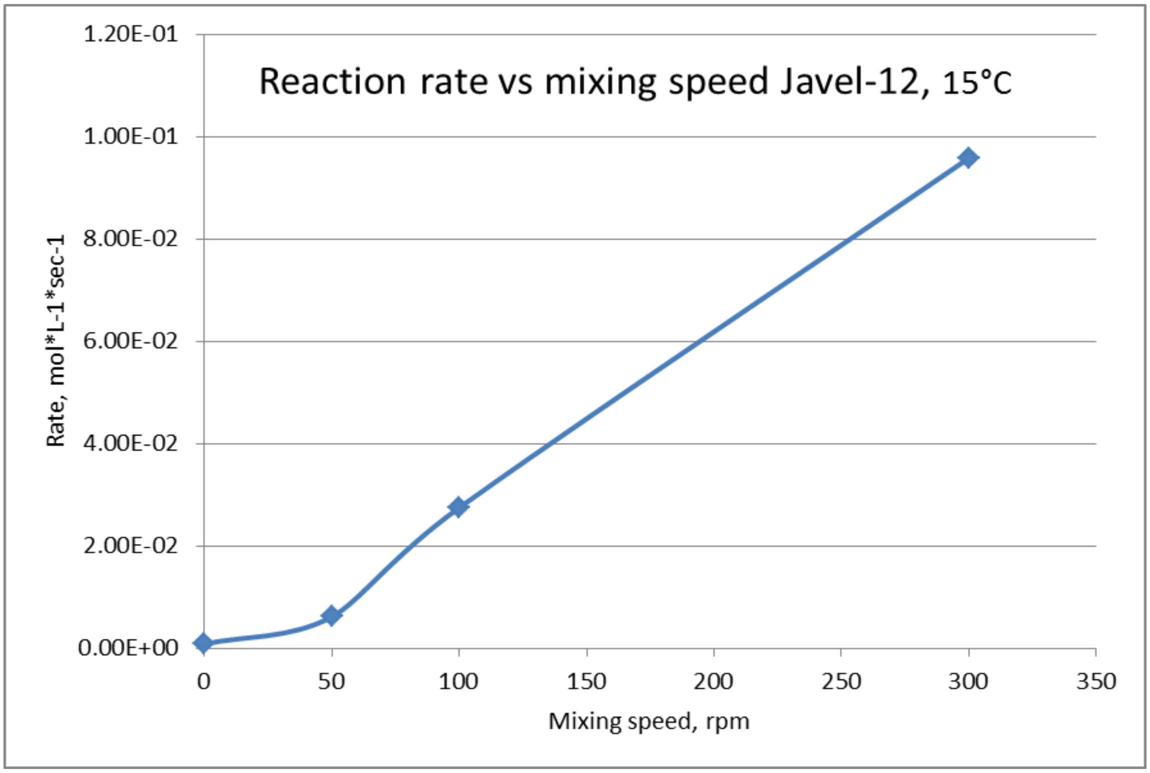


Fig. 65 Initial reaction rate vs. mixing speed for Javel-12 at 15 °C

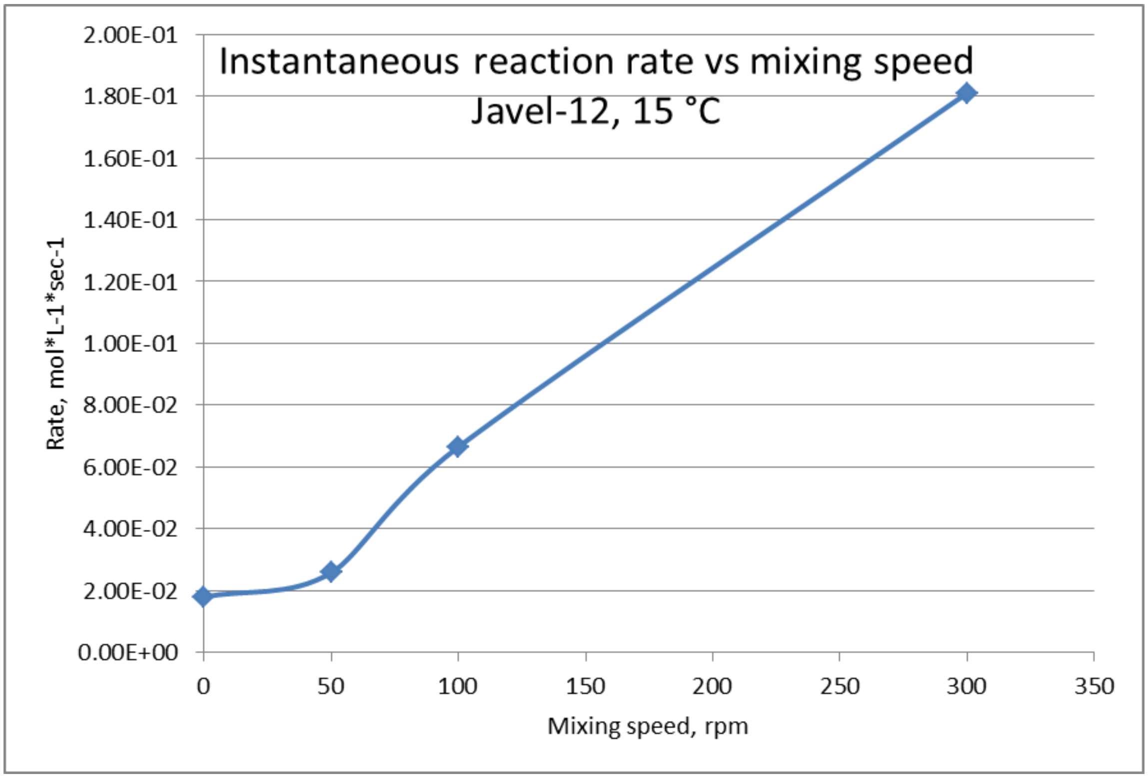


Fig. 66 Instantaneous (maximal point) reaction rate vs. mixing speed for Javel-12 at 15 °C

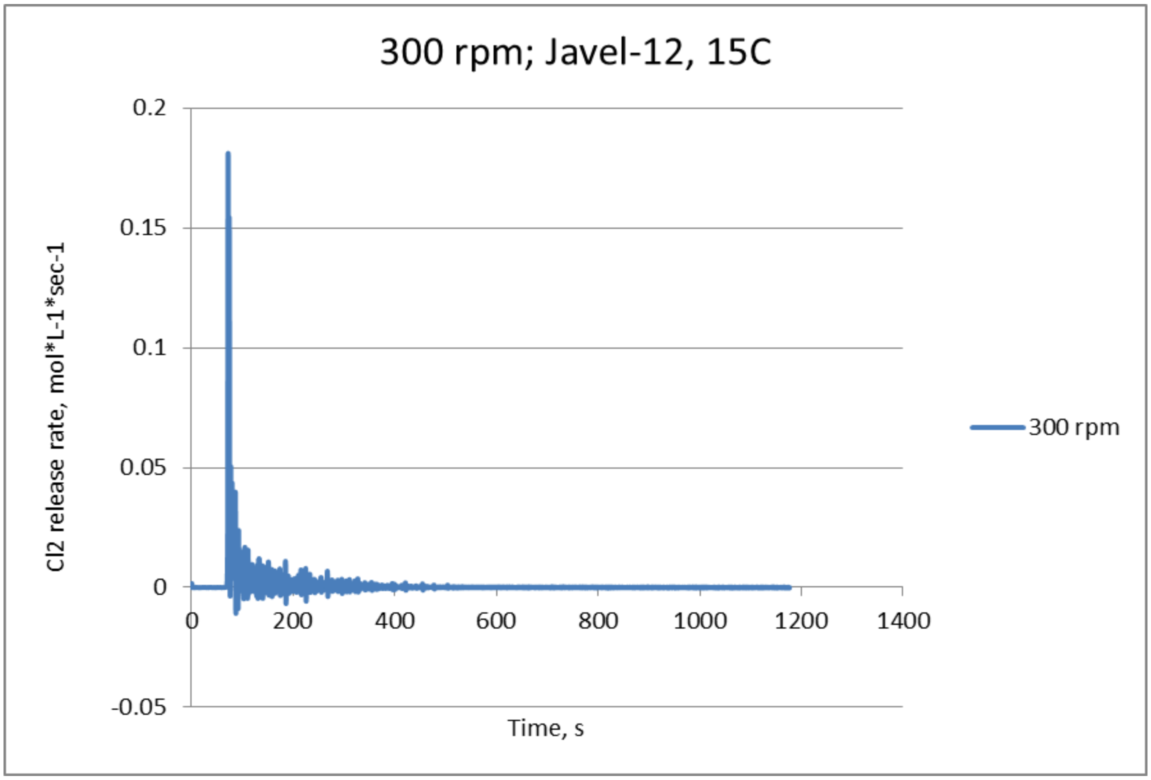


Fig. 67 Instantaneous reaction rate vs. time for Javel-12 at 15 °C at 300 rpm mixing speed

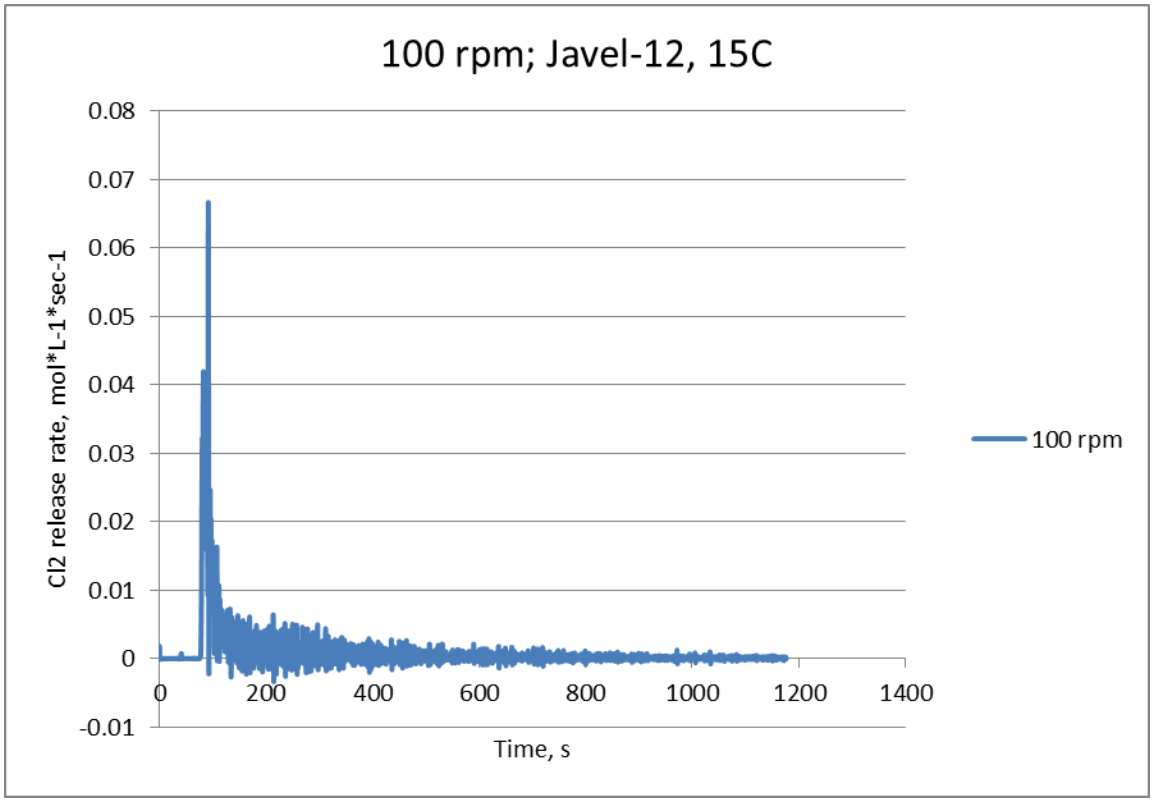


Fig. 68 Instantaneous reaction rate vs. time for Javel-12 at 15 °C at 100 rpm mixing speed

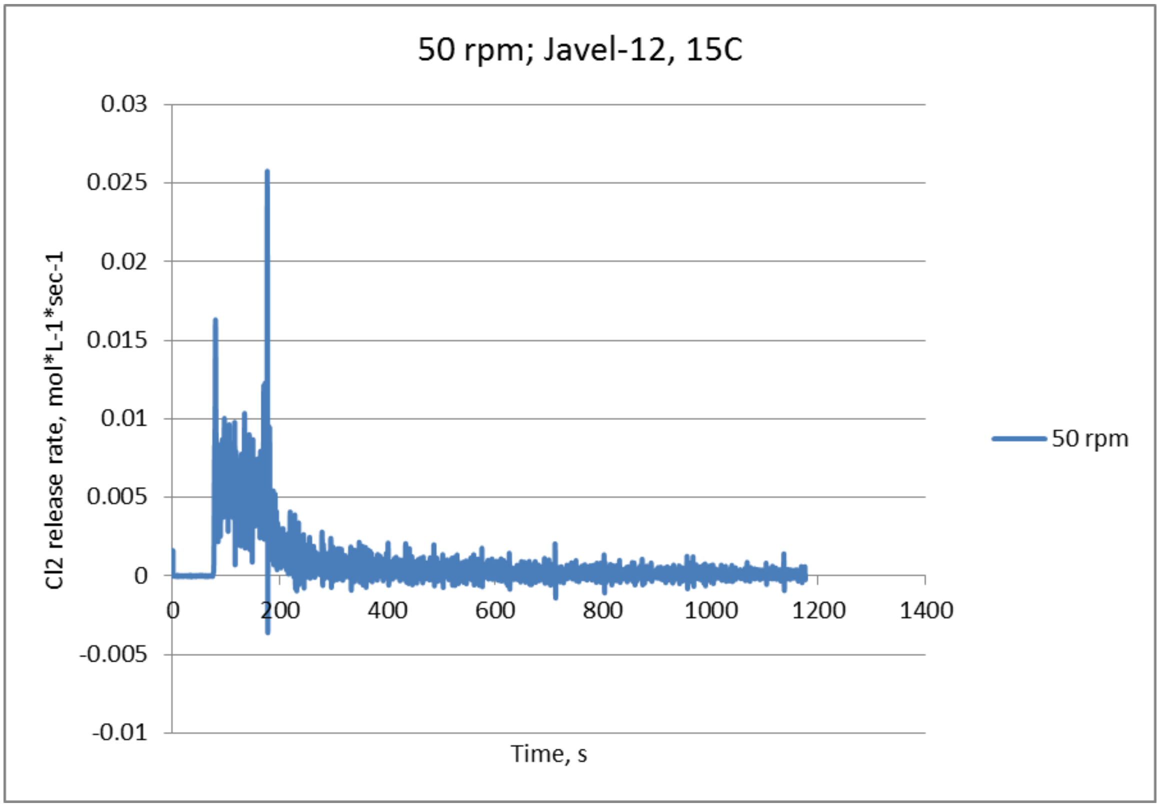


Fig. 69 Instantaneous reaction rate vs. time for Javel-12 at 15 °C at 50 rpm mixing speed

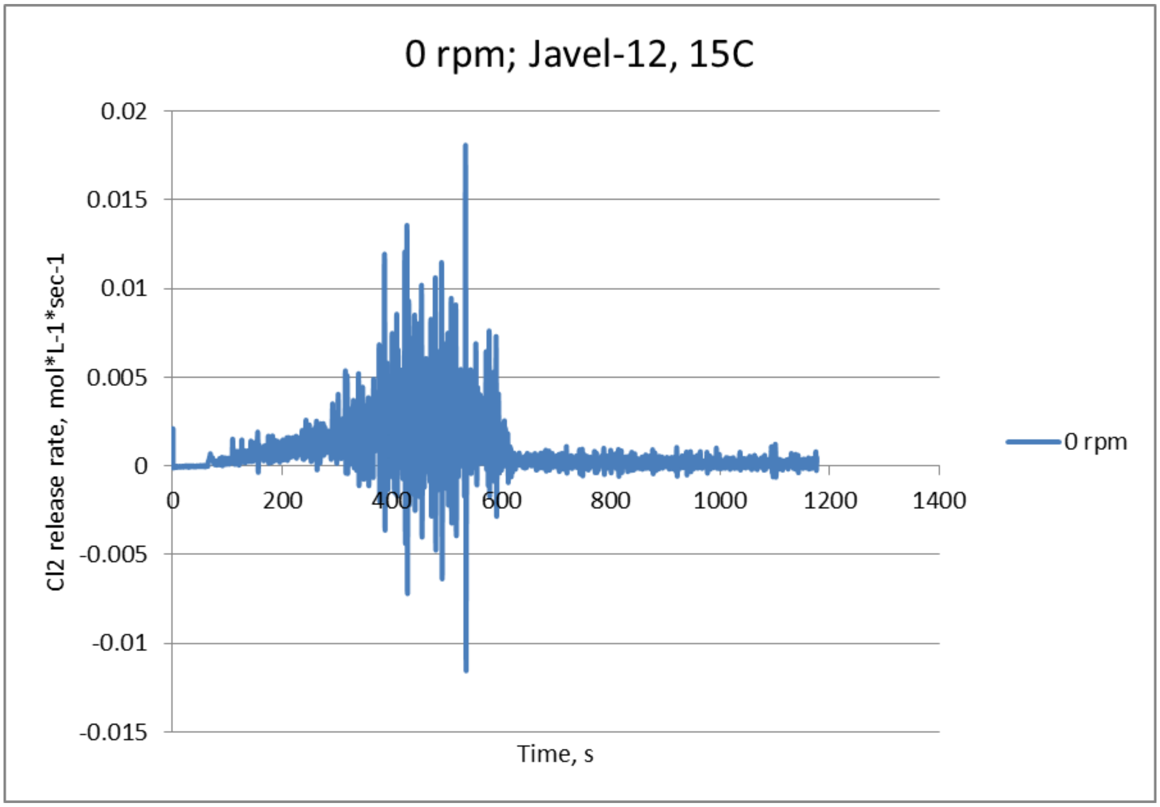


Fig. 70 Instantaneous reaction rate vs. time for Javel-12 at 15 °C at 0 rpm mixing speed

At the zero speed, the instantaneous rate increased gradually and reached maximum at about 10 min. At this time a lot of chlorine bubbles were formed, that resulted in positive and negative “peaks” on the plot.

Javel-12, 22 °C

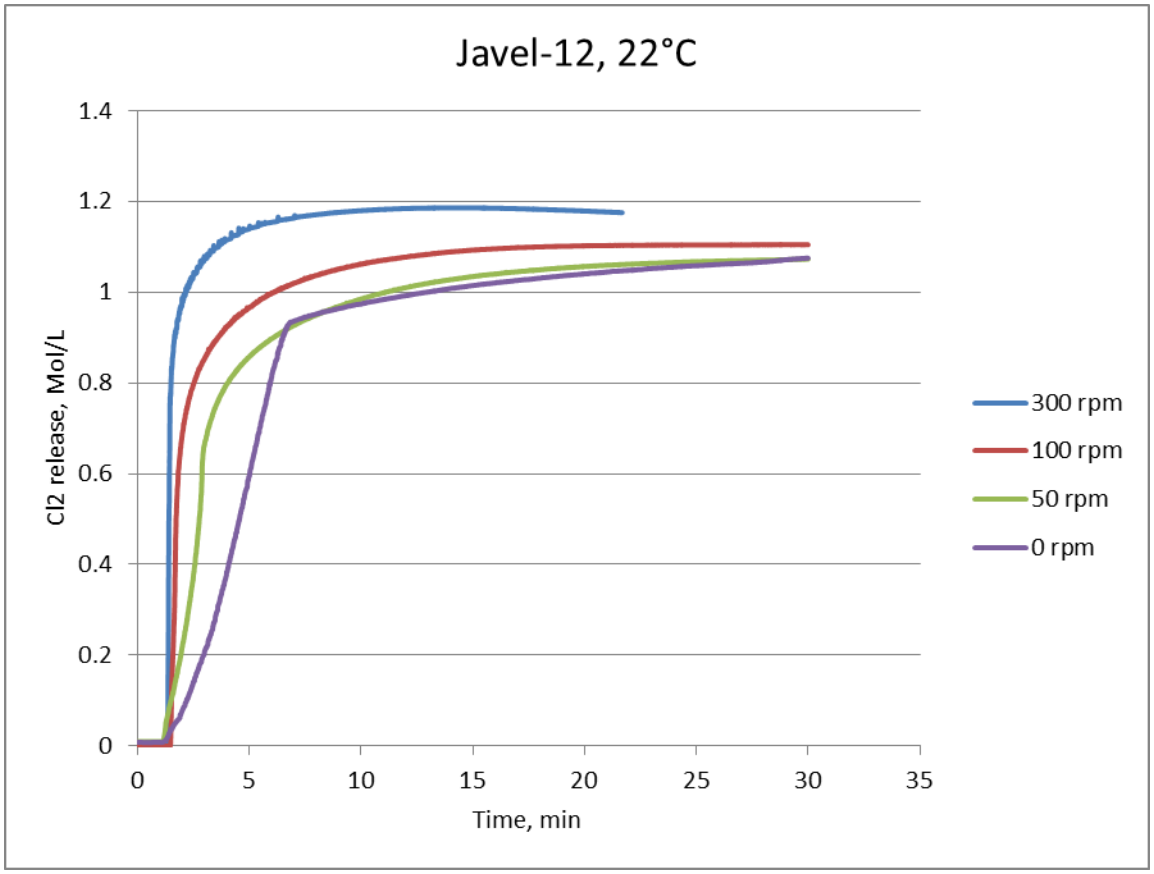


Fig. 71 Chlorine release from Javel-12 product reacted with HCl at 22 °C and different mixing speeds

Table 25. Initial and instantaneous (maximal point) rates of chlorine release from Javel-12 product at 22 °C:

Initial

Speed	Rate
0	2.25E-03
50	3.70E-03
100	2.62E-02
300	1.42E-01

instantaneous

Speed	Rate
0	1.33E-02
50	3.70E-02
100	6.12E-02
300	1.87E-01

At higher temperature; mixing speed influences the reaction rate less, however it remained significant: the difference was 2 to 3 orders of magnitude.

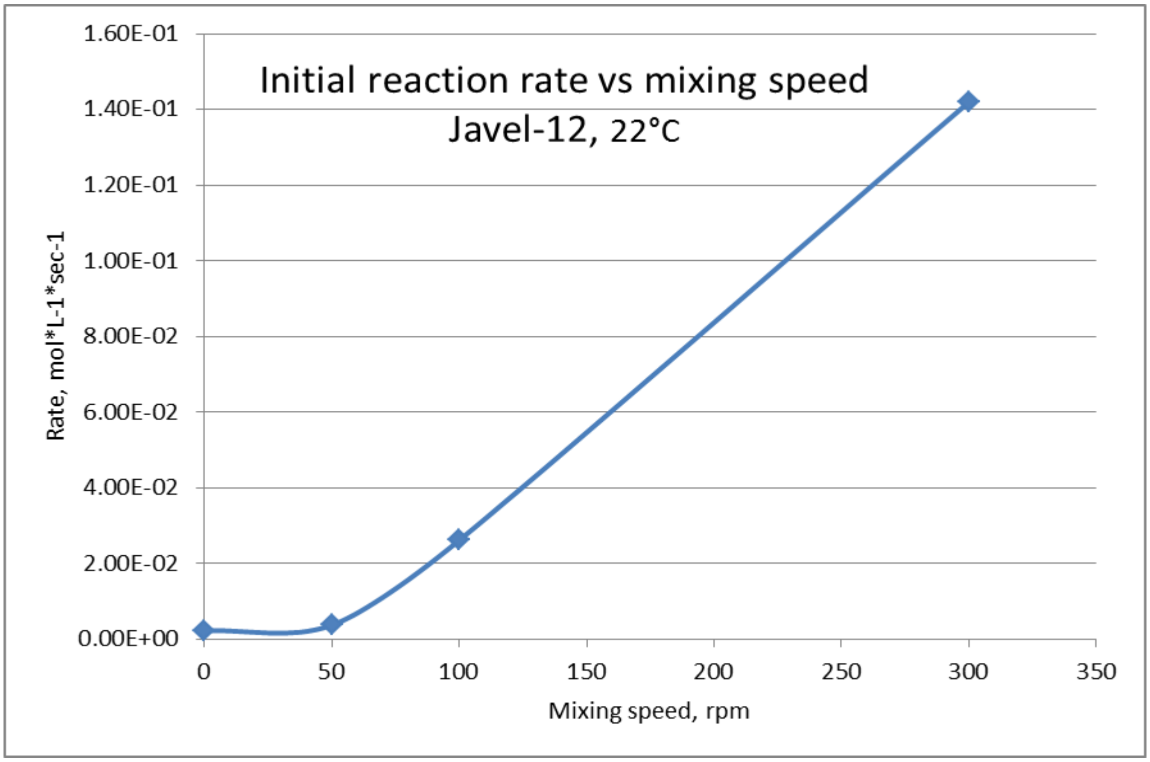


Fig. 72 Initial reaction rate vs. mixing speed for Javel-12 at 22 °C

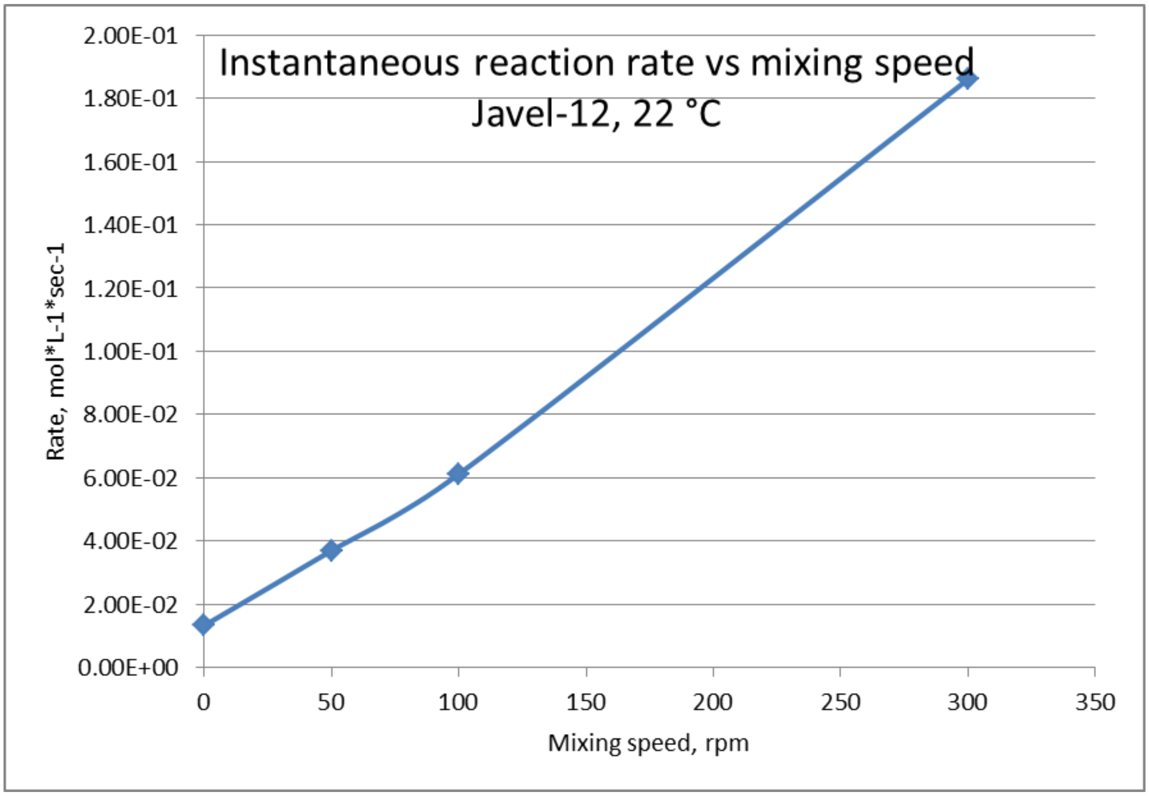


Fig. 73 . Instantaneous (maximal point) reaction rate vs. mixing speed for Javel-12 at 22 °C

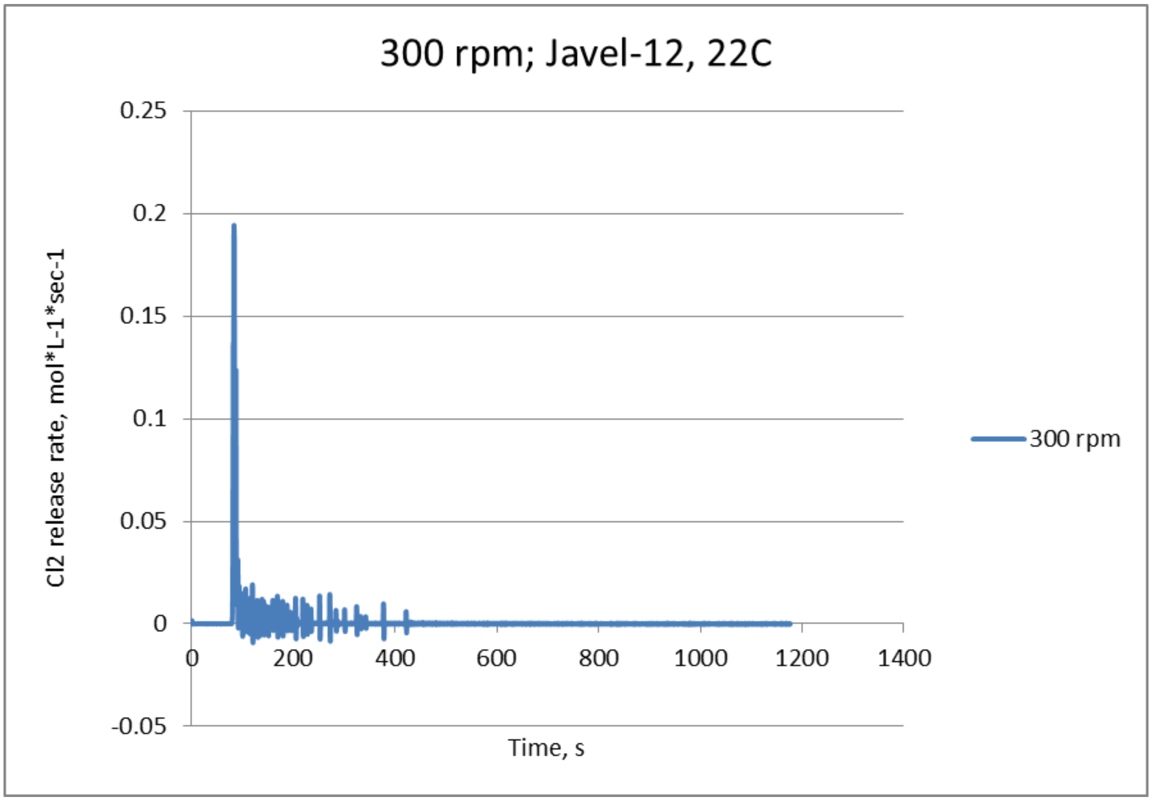


Fig. 74 . Instantaneous reaction rate vs. time for Javel-12 at 22 °C at 300 rpm mixing speed

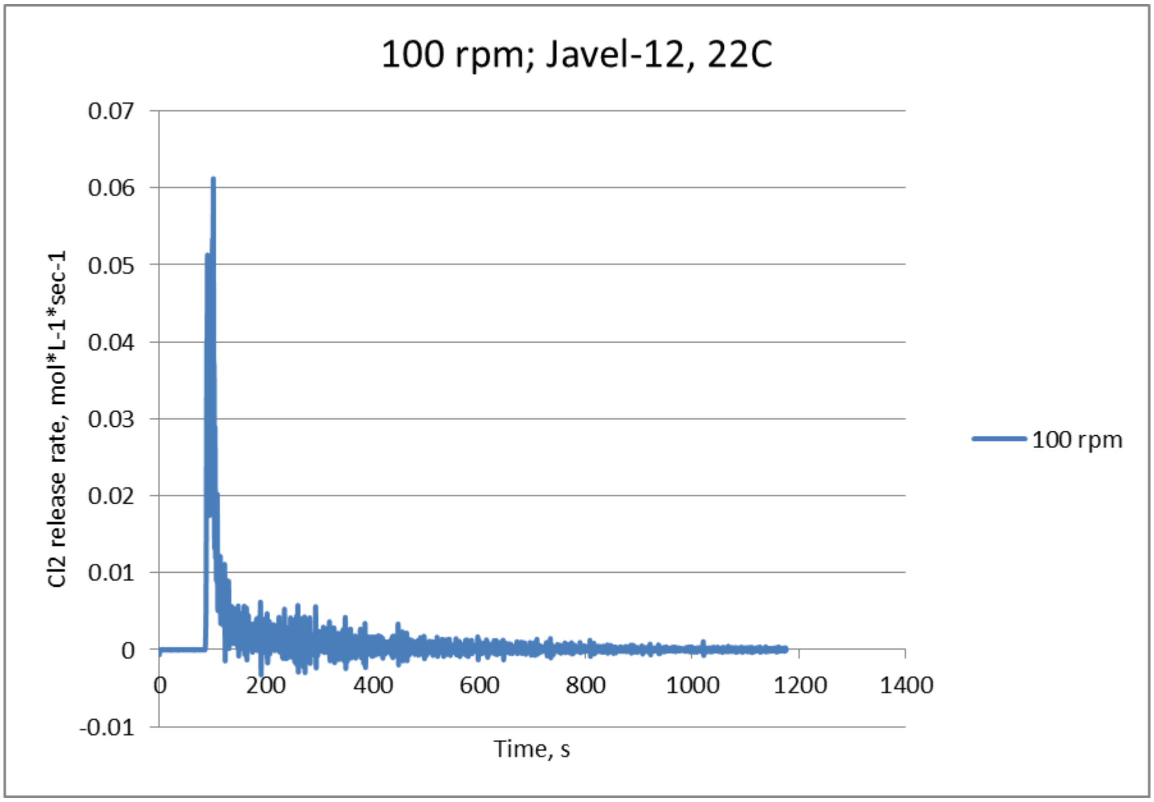


Fig. 75 Instantaneous reaction rate vs. time for Javel-12 at 22 °C at 100 rpm mixing speed

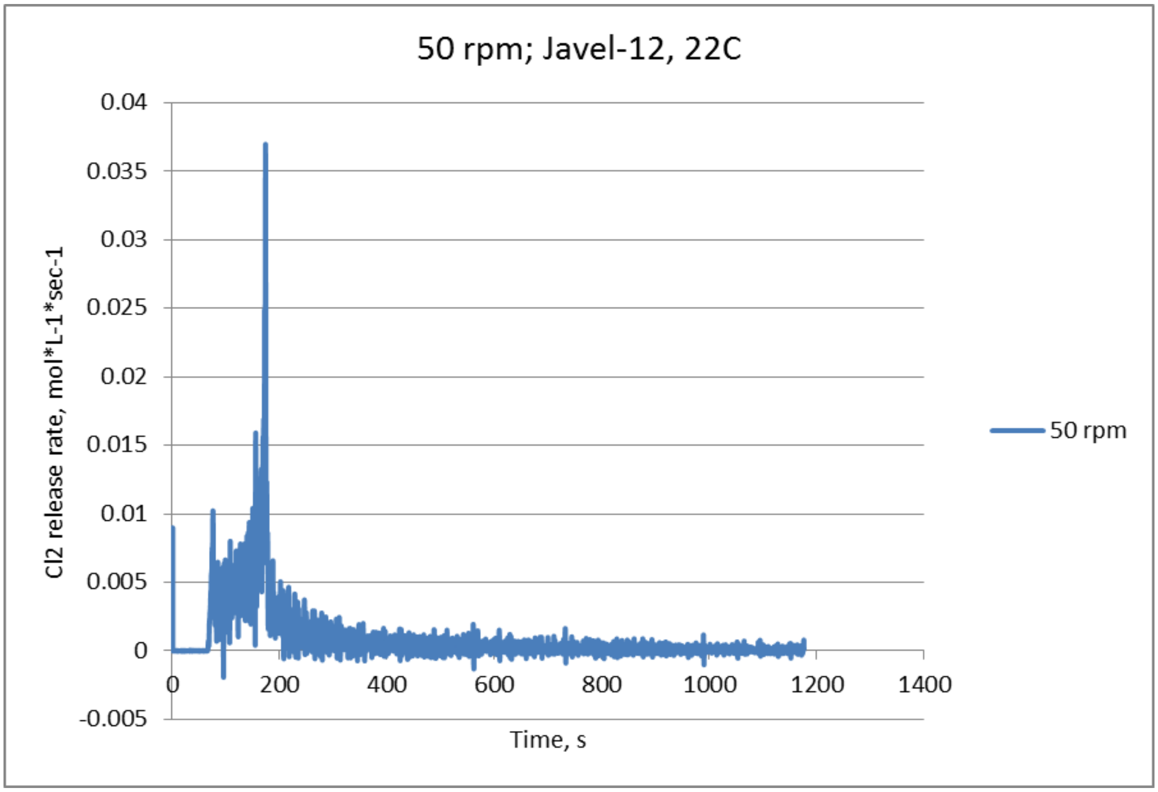


Fig. 76 Instantaneous reaction rate vs. time for Javel-12 at 22 °C at 50 rpm mixing speed

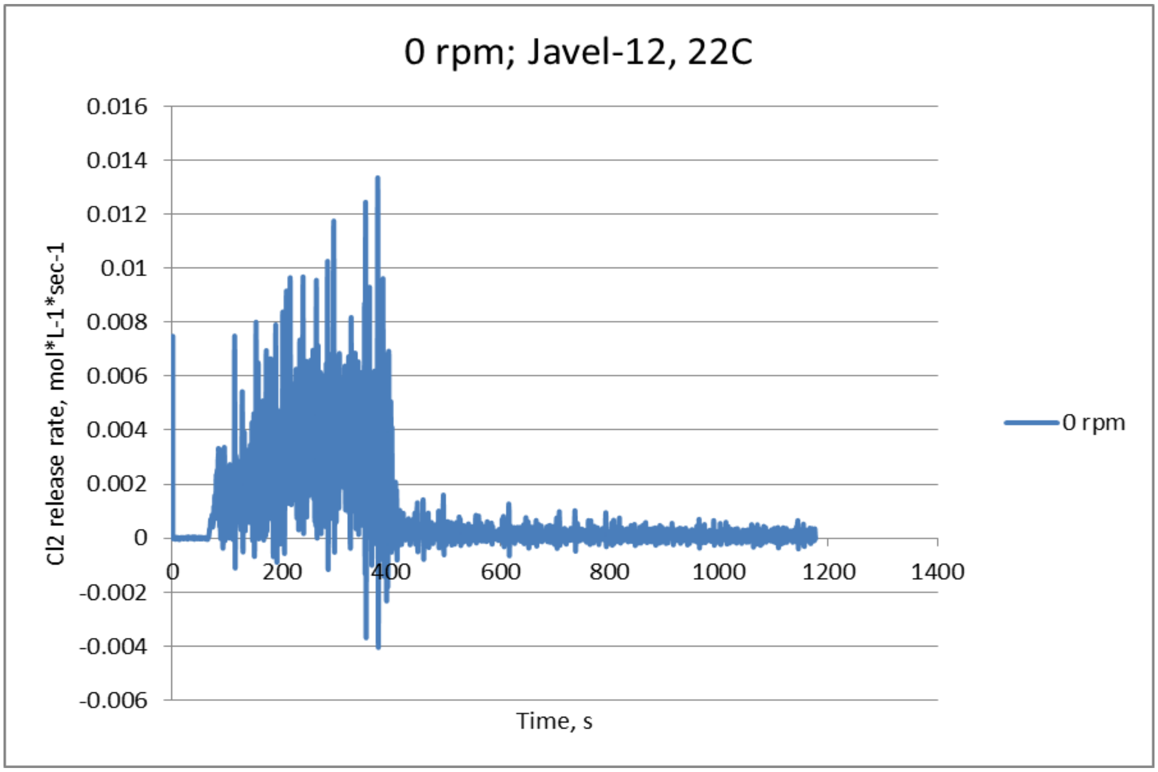


Fig. 77 . Instantaneous reaction rate vs. time for Javel-12 at 22 °C at 0 rpm mixing speed

At zero mixing speed the reaction rate reaches the maximum at about 8 minutes.

Javel – 12 --- 30 °C

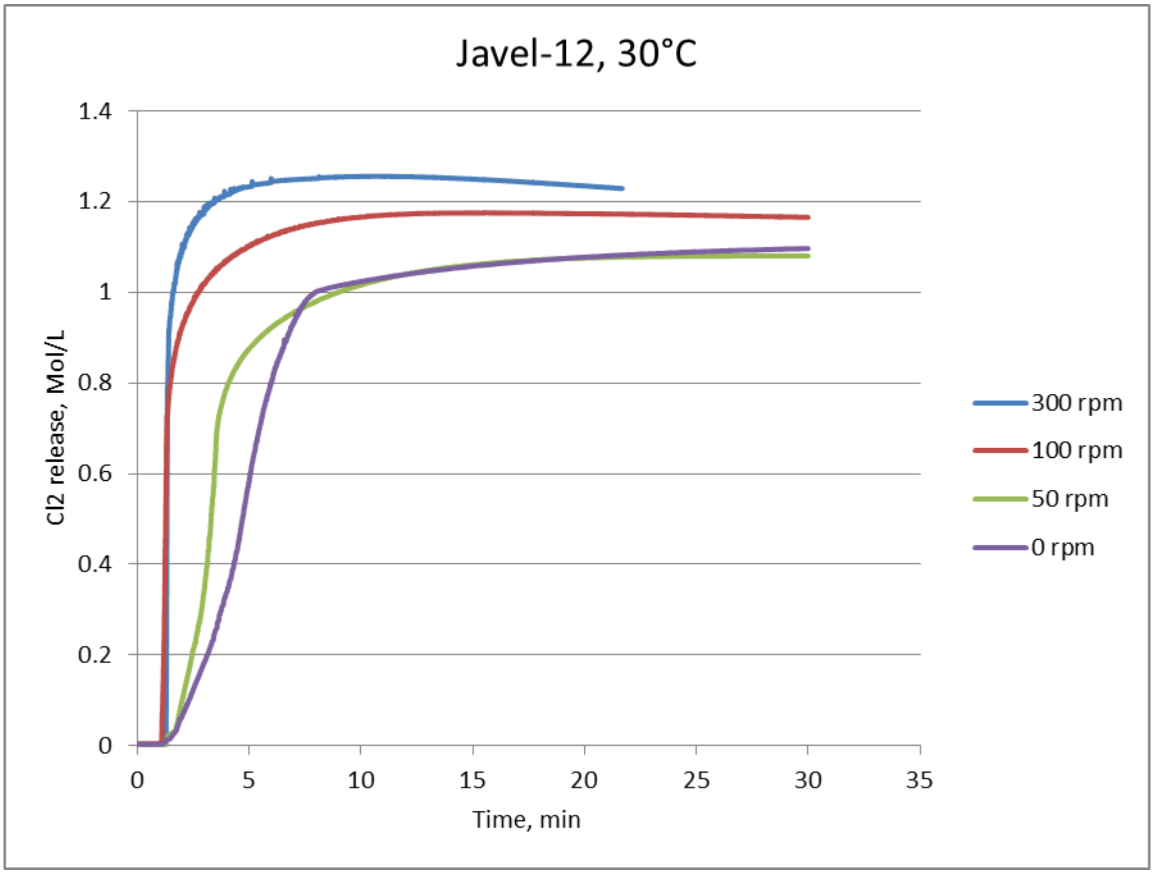


Fig. 78 Chlorine release from Javel-12 product reacted with HCl at 30 °C and different mixing speeds

Table 26. Initial and instantaneous maximal point rates of chlorine release from Javel-12 product at 30 °C:

Initial

Speed	Rate
0	2.05E-03
50	3.88E-03
100	5.85E-02
300	1.78E-01

instantaneous

Speed	Rate
0	1.00E-02
50	3.72E-02
100	1.02E-01
300	2.61E-01

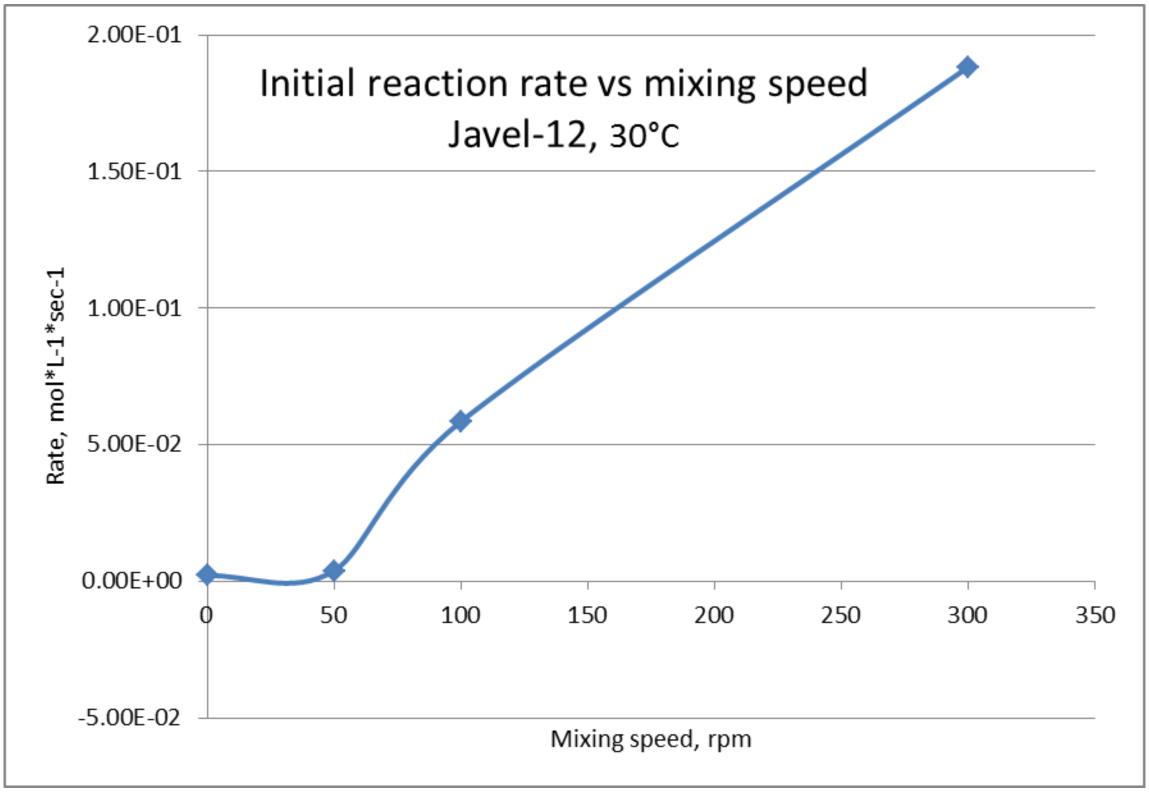


Fig. 79 Initial reaction rate vs. mixing speed for Javel-12 at 30 °C

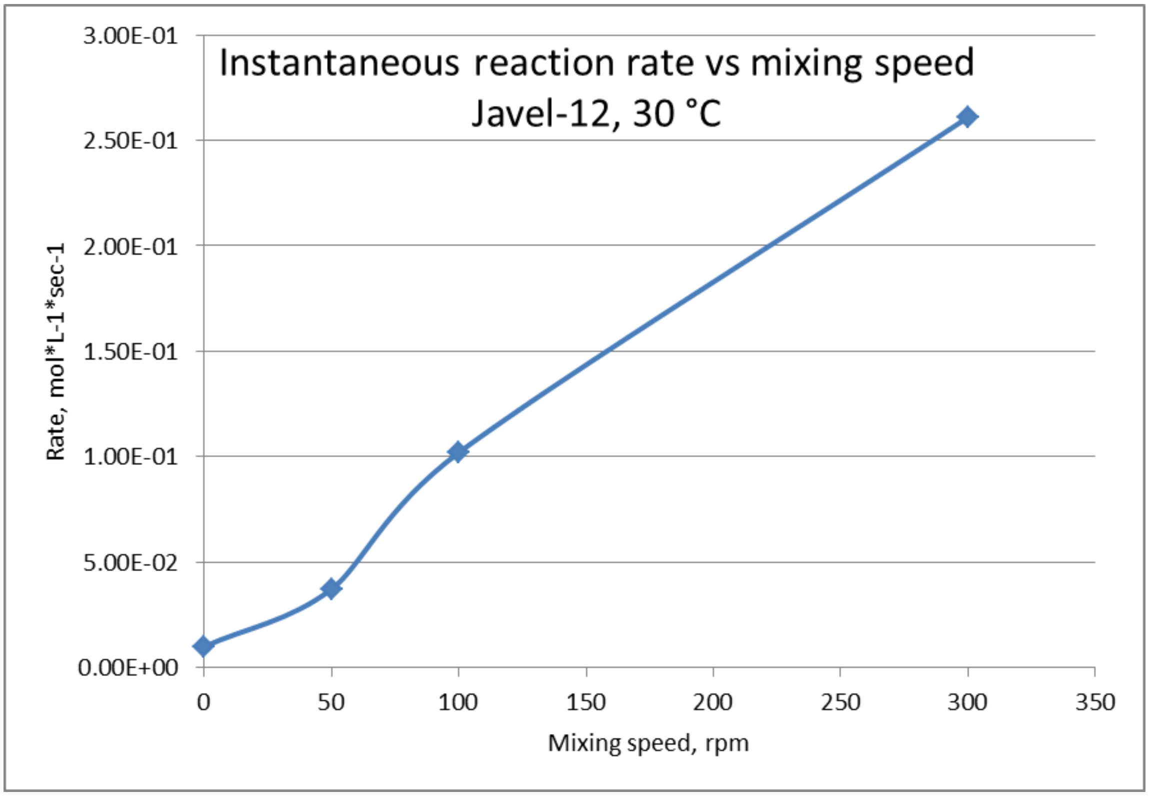


Fig. 80 Instantaneous (maximal point) reaction rate vs. mixing speed for Javel-12 at 30 °C

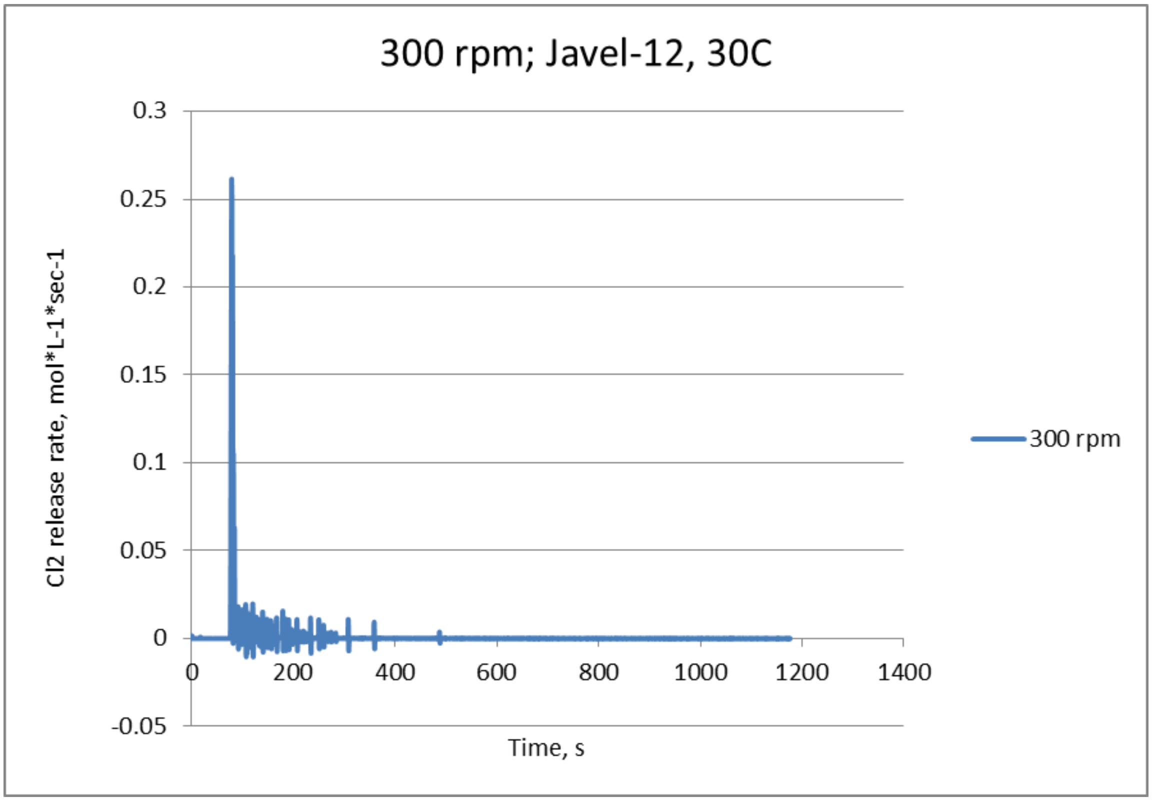


Fig. 81 Instantaneous reaction rate vs. time for Javel-12 at 30 °C at 300 rpm mixing speed

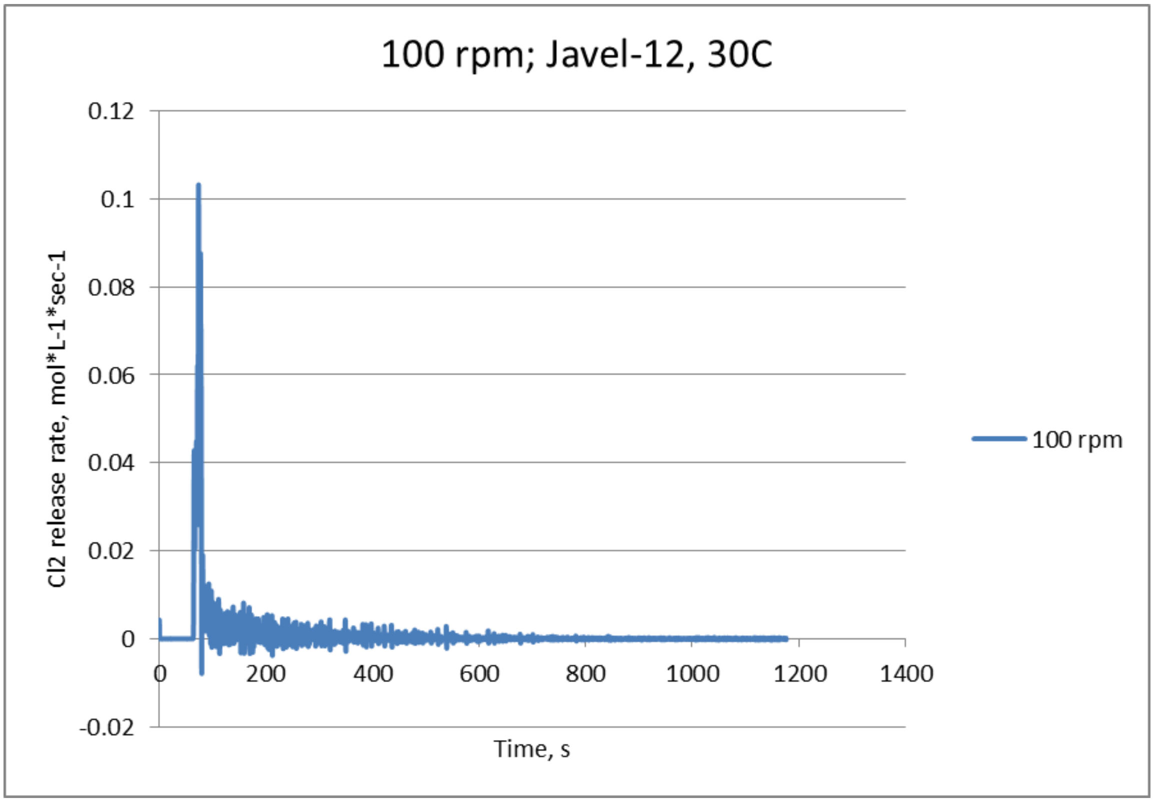


Fig. 82 Instantaneous reaction rate vs. time for Javel-12 at 30 °C at 100 rpm mixing speed

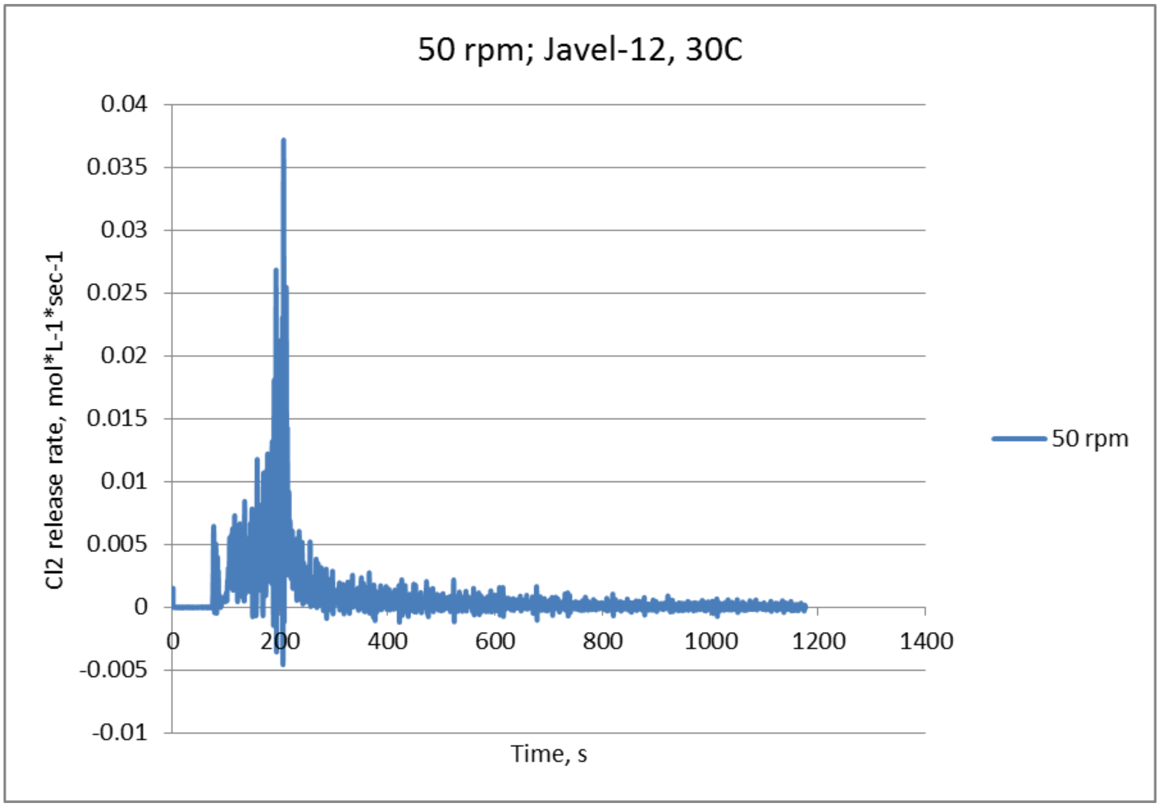


Fig. 83 Instantaneous reaction rate vs. time for Javel-12 at 30 °C at 50 rpm mixing speed

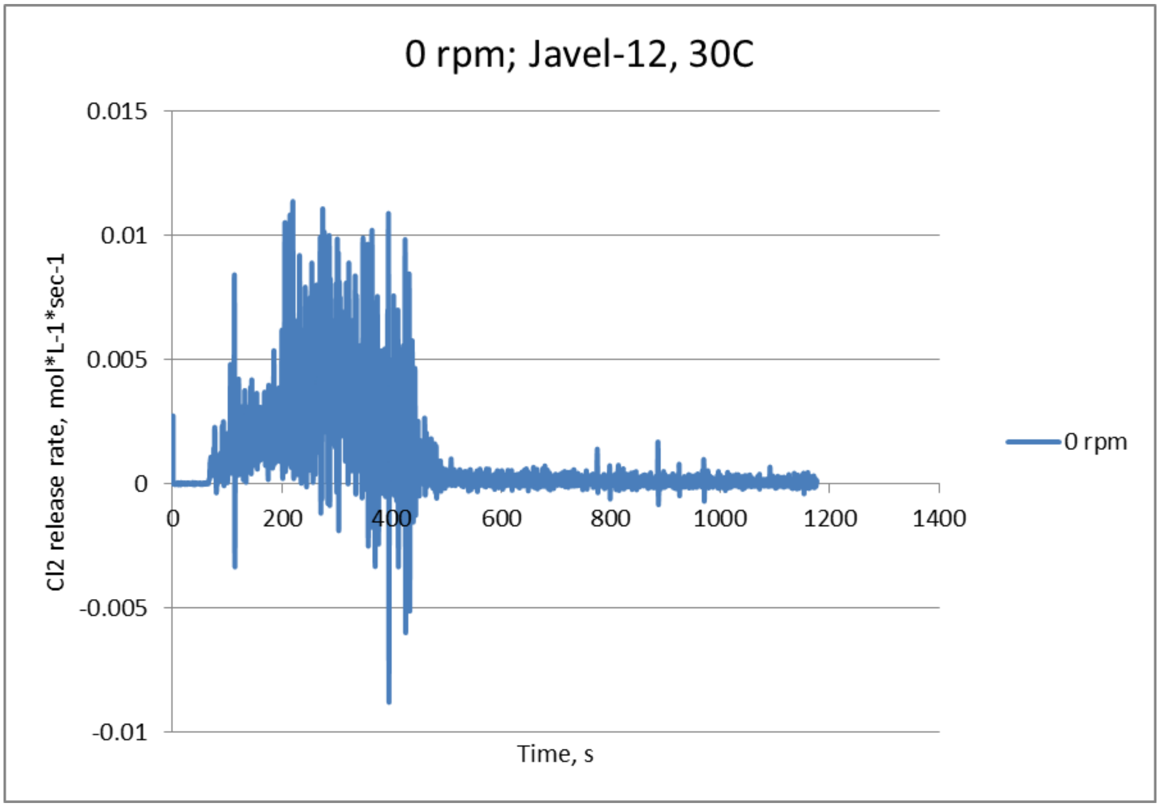


Fig. 84 Instantaneous reaction rate vs. time for Javel-12 at 30 °C at 0 rpm mixing speed

4.4.1.1. Arrhenius Parameters for Javel-12:

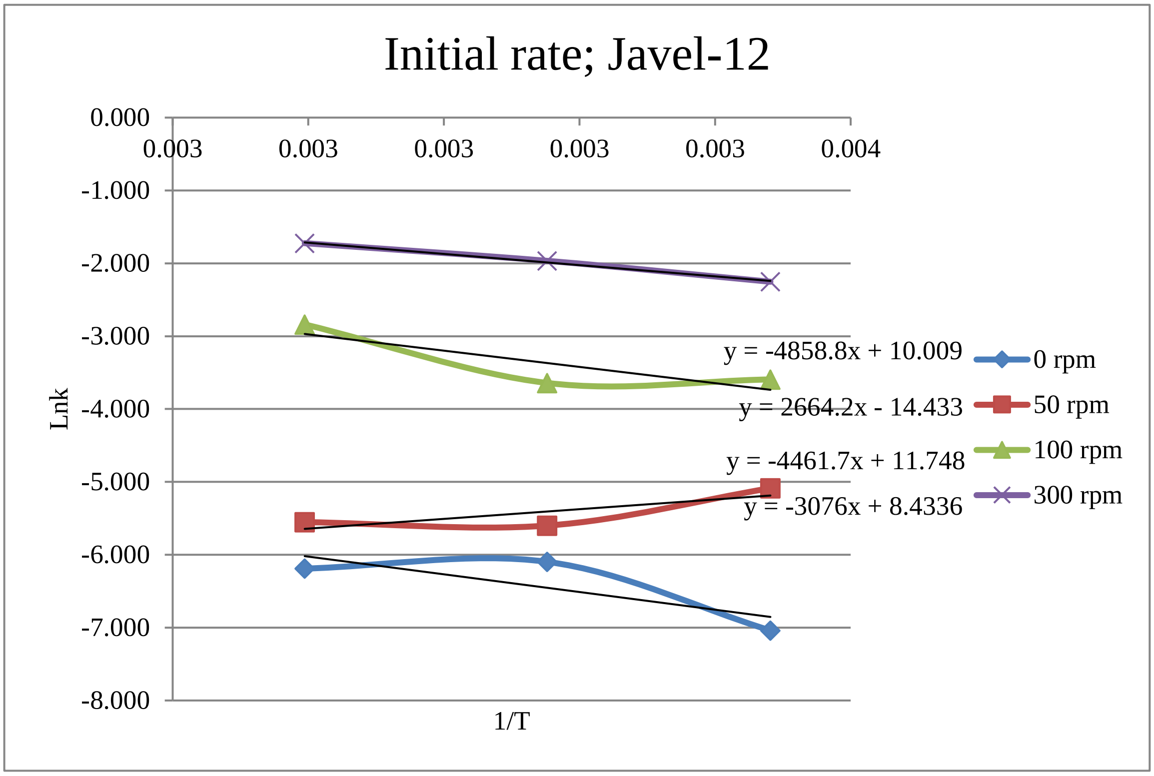


Fig. 85 Arrhenius plots for Javel-12 – initial rate

Table 27. Initial rate kinetic parameters for Javel-12:

Initial k

t	0 rpm	50 rpm	100 rpm	300 rpm
15	8.77E-04	6.18E-03	2.75E-02	1.05E-01
22	2.25E-03	3.70E-03	2.62E-02	1.40E-01
30	2.05E-03	3.88E-03	5.85E-02	1.78E-01

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.003	-7.039	-5.086	-3.594	-2.253
0.003	-6.097	-5.599	-3.642	-1.966
0.003	-6.190	-5.552	-2.839	-1.724
M =	-4858.800	2664.200	-4461.700	-3076.000
B =	10.000	14.430	11.740	8.434
E_a =	40.396	-22.150	37.095	25.574
A=	2.203E+04	1.849E+06	1.255E+05	4.599E+03

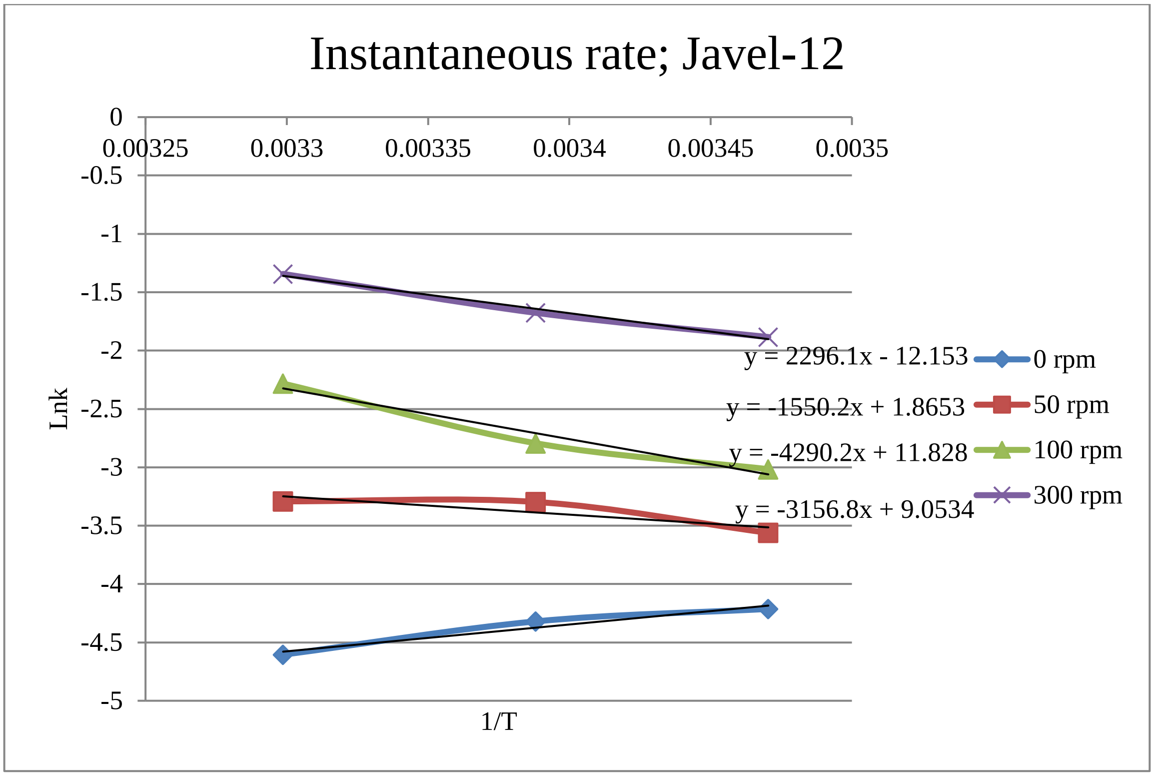


Fig. 86 Arrhenius plots for Javel-12 – instantaneous maximal point rate

Table 28. Instantaneous rate kinetic parameters for Javel-12:

Instant

t, C	0 rpm	50 rpm	100 rpm	300 rpm
15	1.48E-02	2.84E-02	4.90E-02	1.52E-01
22	1.33E-02	3.70E-02	6.12E-02	1.87E-01
30	1.00E-02	3.72E-02	1.02E-01	2.61E-01

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.00347	-4.21313	-3.56137	-3.01593	-1.88387
0.00339	-4.31999	-3.29684	-2.79361	-1.67665
0.00330	-4.60517	-3.29145	-2.28278	-1.34323
M =	2296.1	-1550.2	-4290.2	-3156.8
B =	12.15	1.865	11.828	9.053
E_a =	-19.090	12.888	35.669	26.246
A=	1.891E+05	6.456E+00	1.370E+05	8.544E+03

As can be seen, the energy of activation parameter (Ea) becomes negative at a low mixing speed, indicating that the process is regulated by mixing. This means that the mixing and the diffusion become rate-limiting steps of the reaction and it is not controlled by thermodynamics as it was at a high speeds. At low mixing speeds (0 to 50 rpm) the Arrhenius parameters lose their thermodynamic meaning, however they may be used as empirical values that describe overall system response to the temperature change.

4.4.2. Ultra San

Ultra san --- 15°C

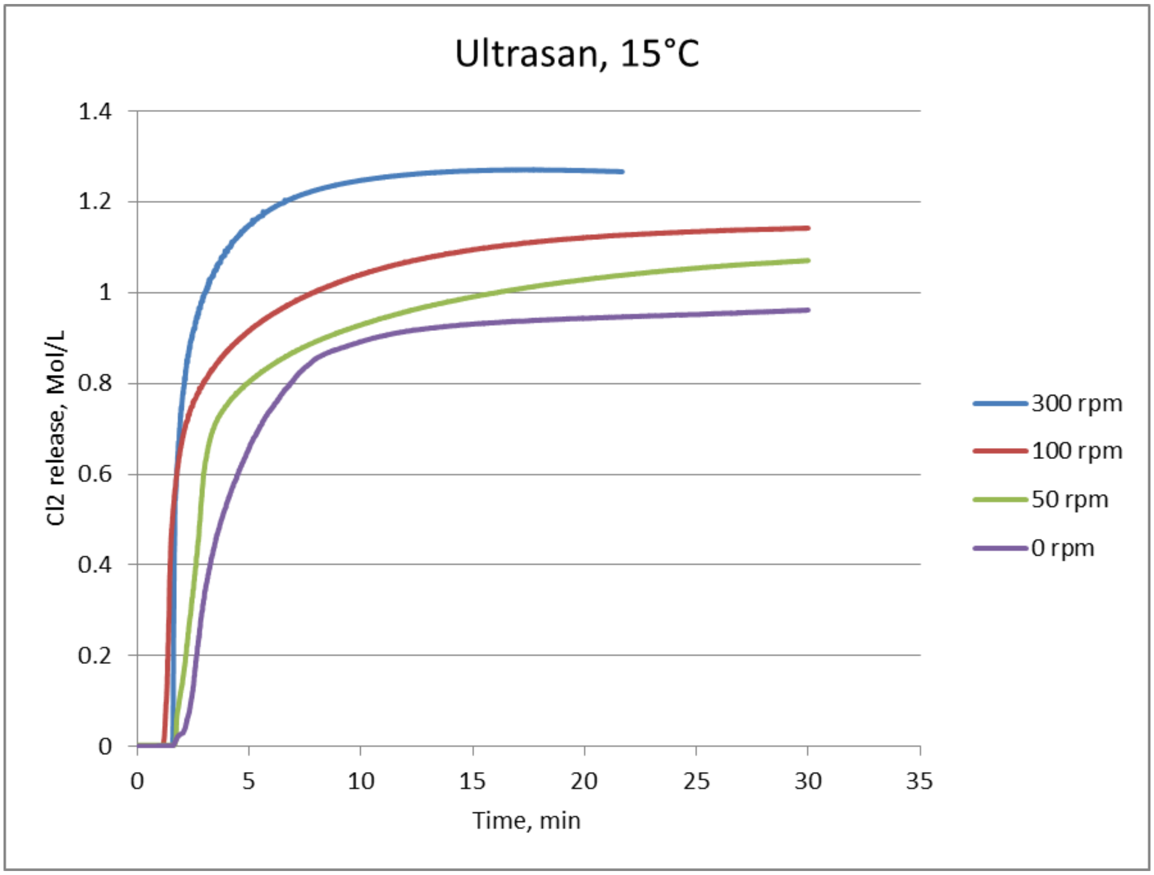


Fig. 87 Chlorine release from Ultrasan product reacted with HCl at 15 °C and different mixing speeds

Table 29. Initial and instantaneous maximal point rates of chlorine release from Ultrasan product at 15 °C:

Initial	
Speed	Rate
0	6.53E-03
50	6.75E-03
100	2.38E-02
300	9.13E-02

instantaneous	
Speed	Rate
0	1.48E-02
50	2.84E-02
100	4.90E-02
300	1.57E-01

In the case of Ultra San product; the reaction rate strongly depends on the mixing speed.

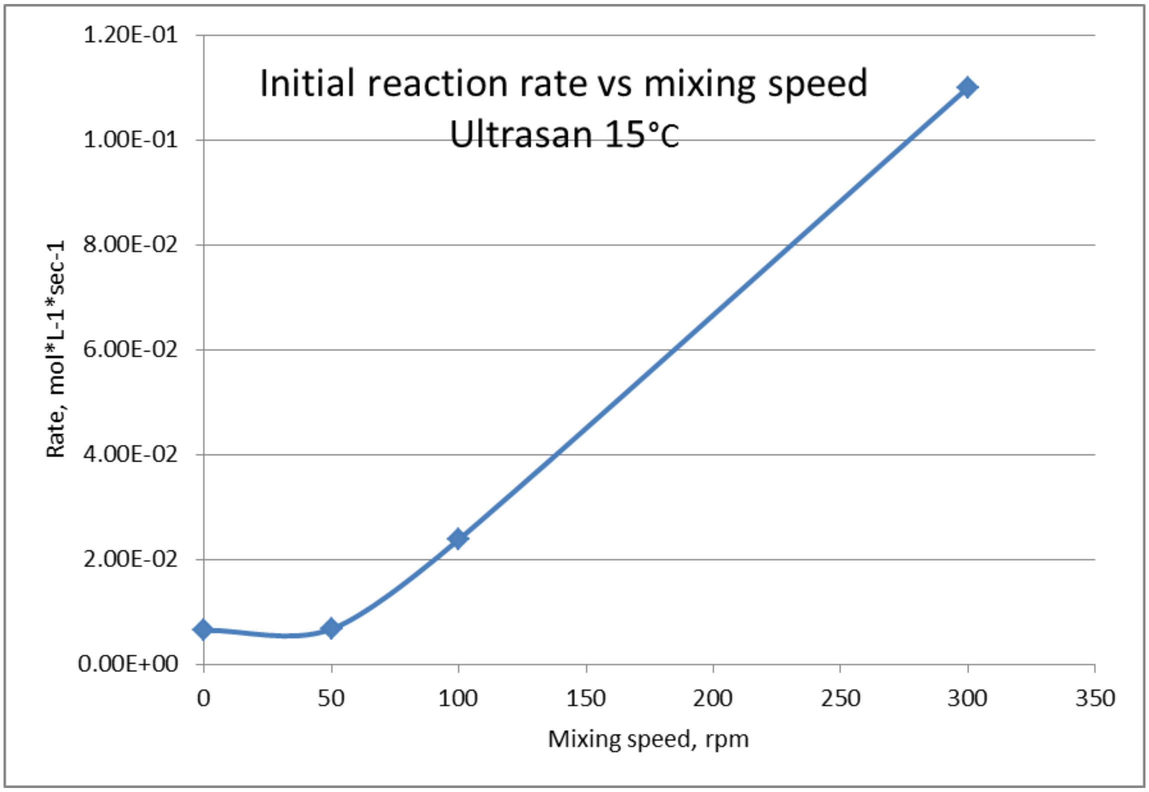


Fig. 88 Initial reaction rate vs. mixing speed for Ultrasan at 15 °C

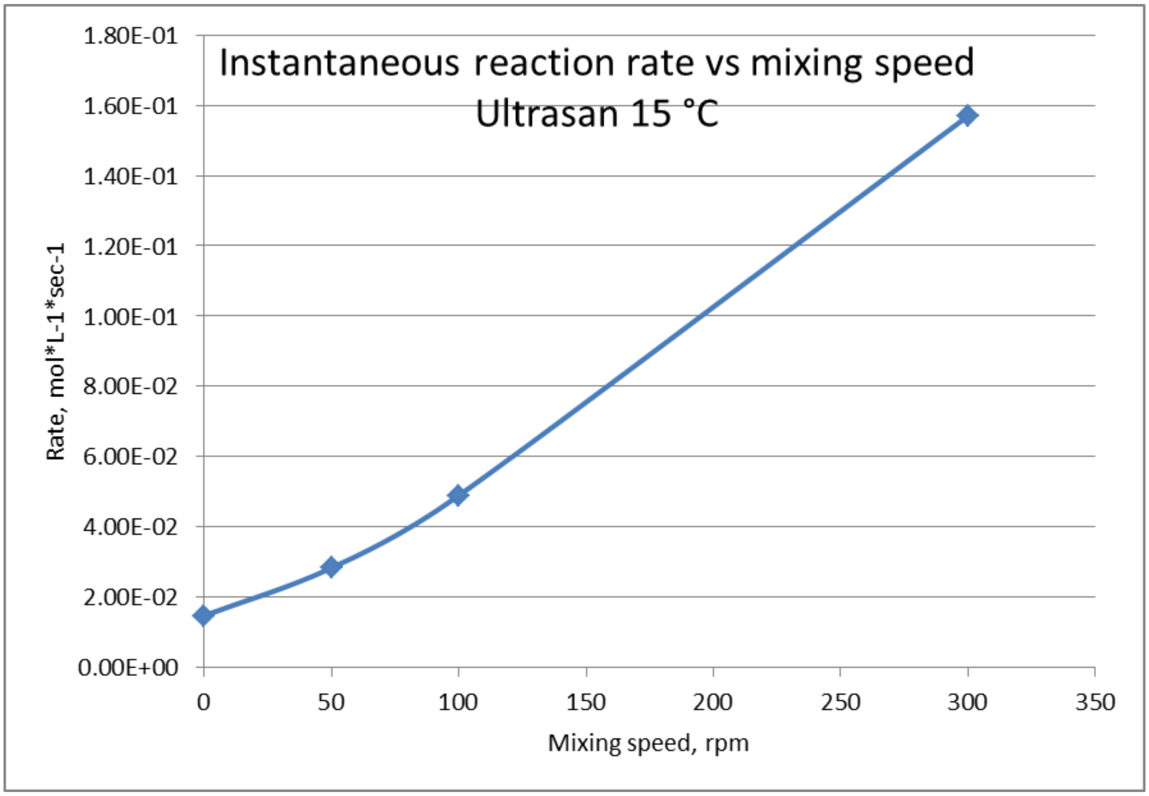


Fig. 89 Instantaneous (maximal point) reaction rate vs. mixing speed for Ultrasan at 15 °C

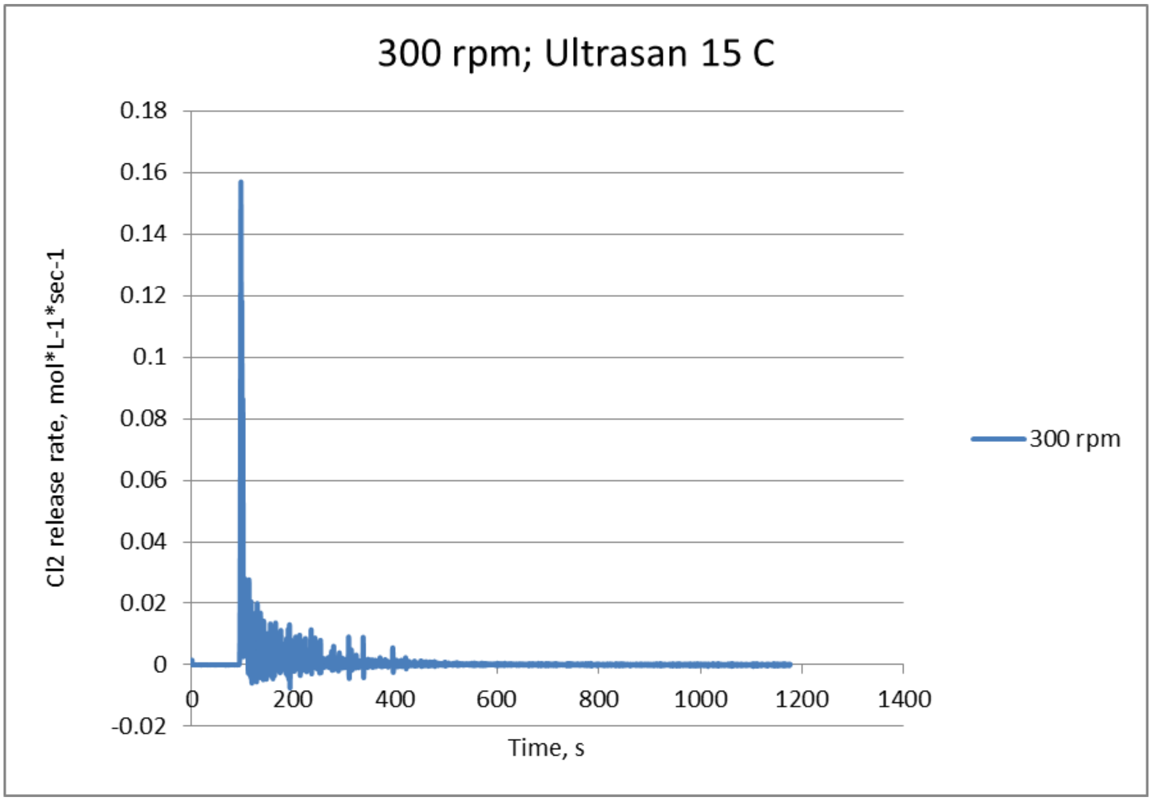


Fig. 90 Instantaneous reaction rate vs. time for Ultrasan at 15 °C at 300 rpm mixing speed

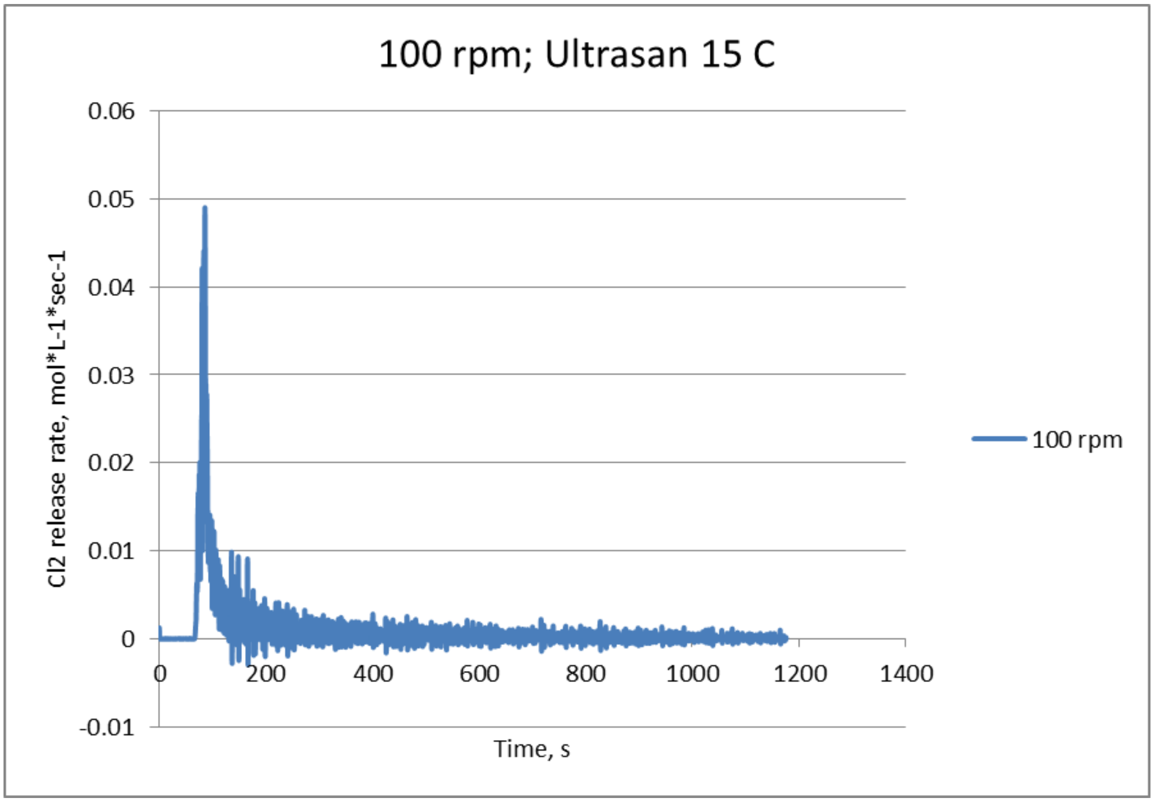


Fig. 91 Instantaneous reaction rate vs. time for Ultrasan at 15 °C at 100 rpm mixing speed

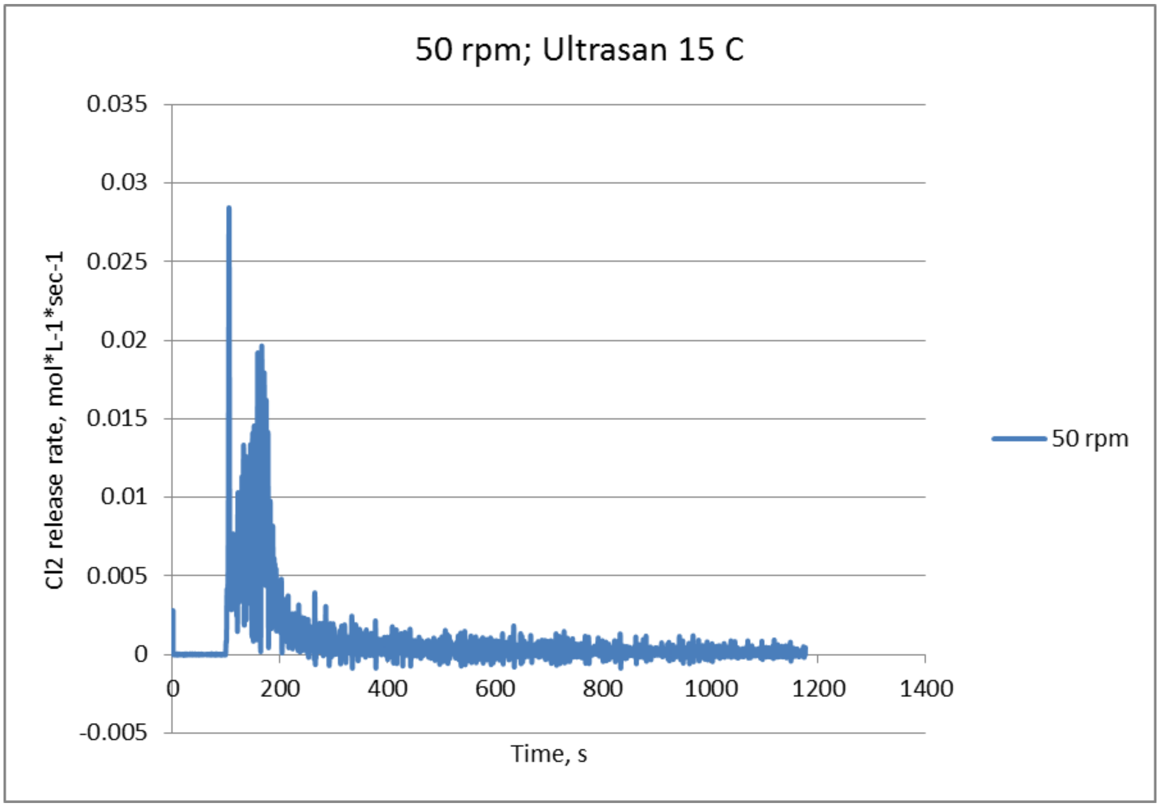


Fig. 92 Instantaneous reaction rate vs. time for Ultrasan at 15 °C at 50 rpm mixing speed

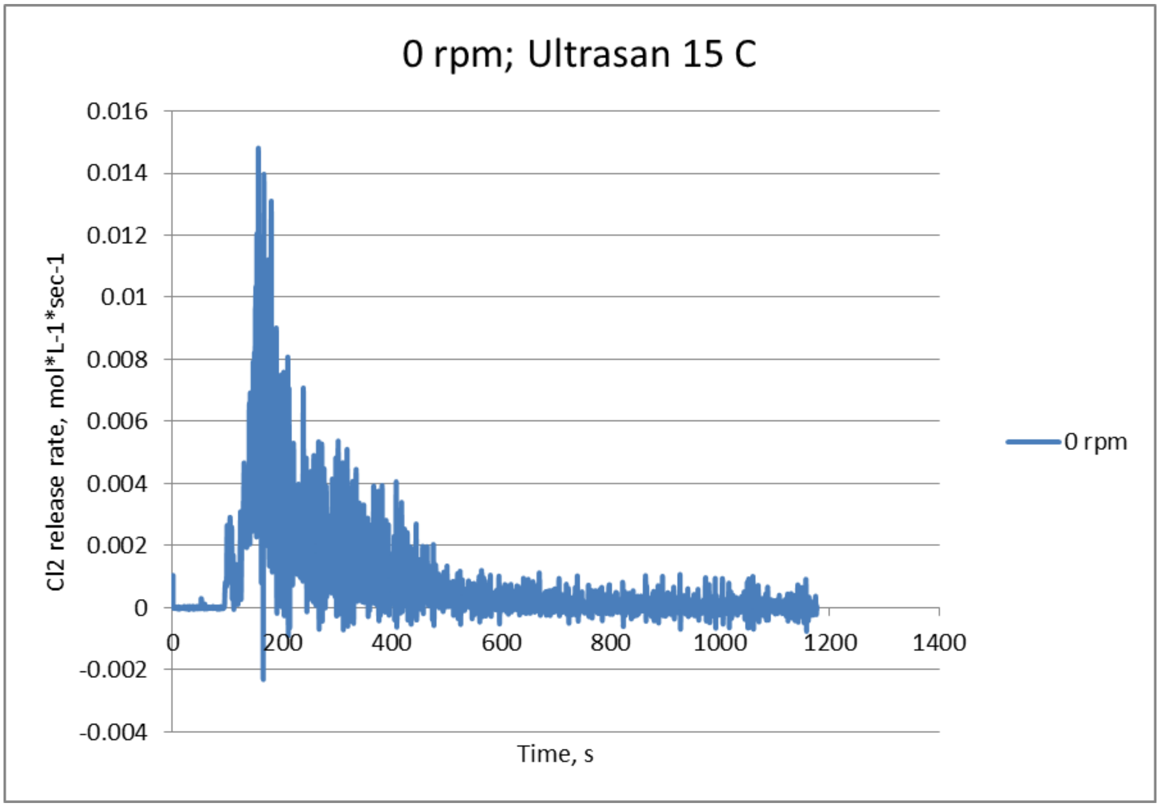


Fig. 93 Instantaneous reaction rate vs. time for Ultrasan at 15 °C at 0 rpm mixing speed

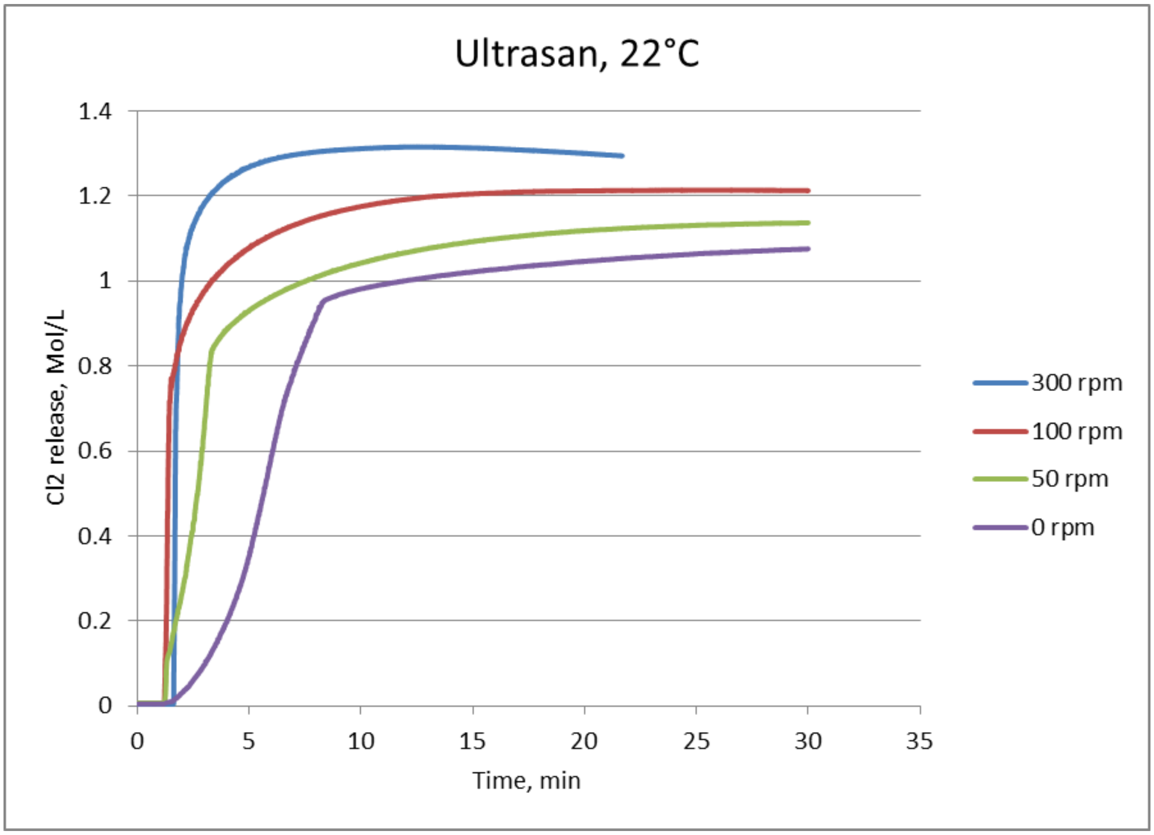


Fig. 94 Chlorine release from Ultrasan product reacted with HCl at 22 °C and different mixing speeds

Table 30. Initial and instantaneous maximal point rates of chlorine release from Ultrasan product at 22 °C:

Initial

Speed	Rate
0	1.17E-03
50	4.02E-03
100	6.05E-02
300	1.20E-01

instantaneous

Speed	Rate
0	1.10E-02
50	3.20E-02
100	9.90E-02
300	1.67E-01

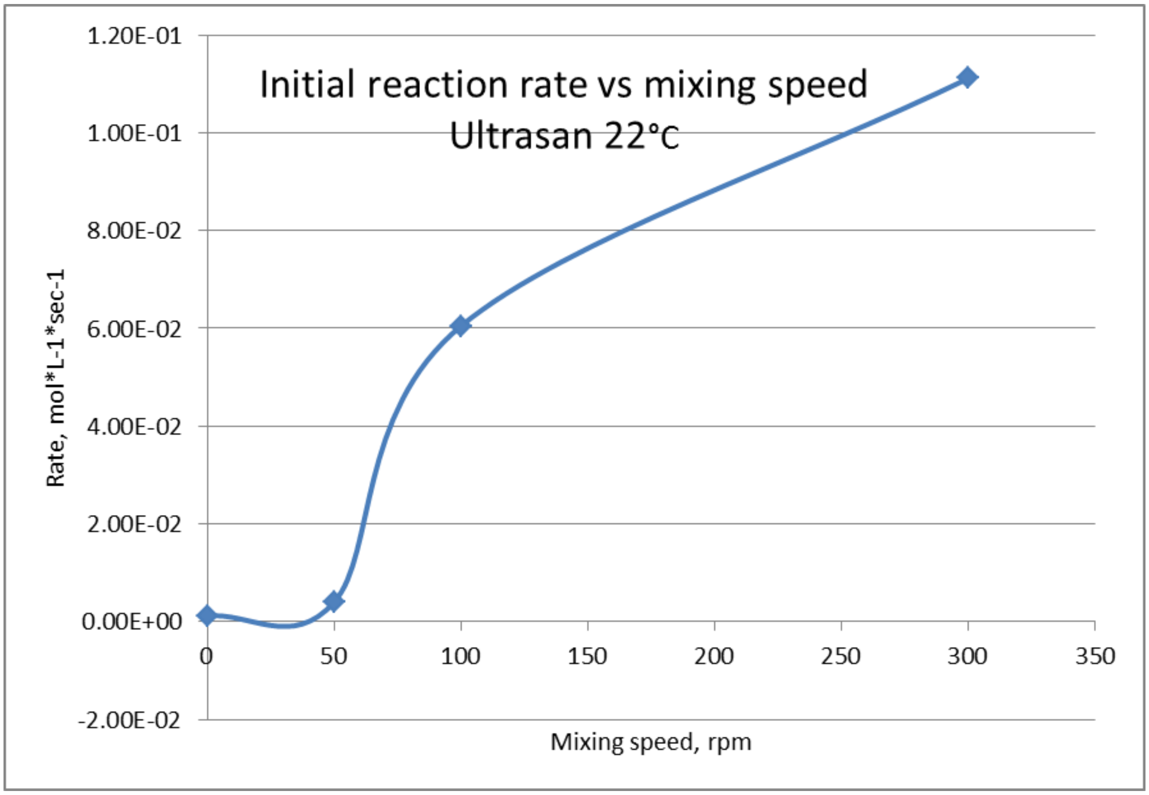


Fig. 95 Initial reaction rate vs. mixing speed for Ultrasan at 22 °C

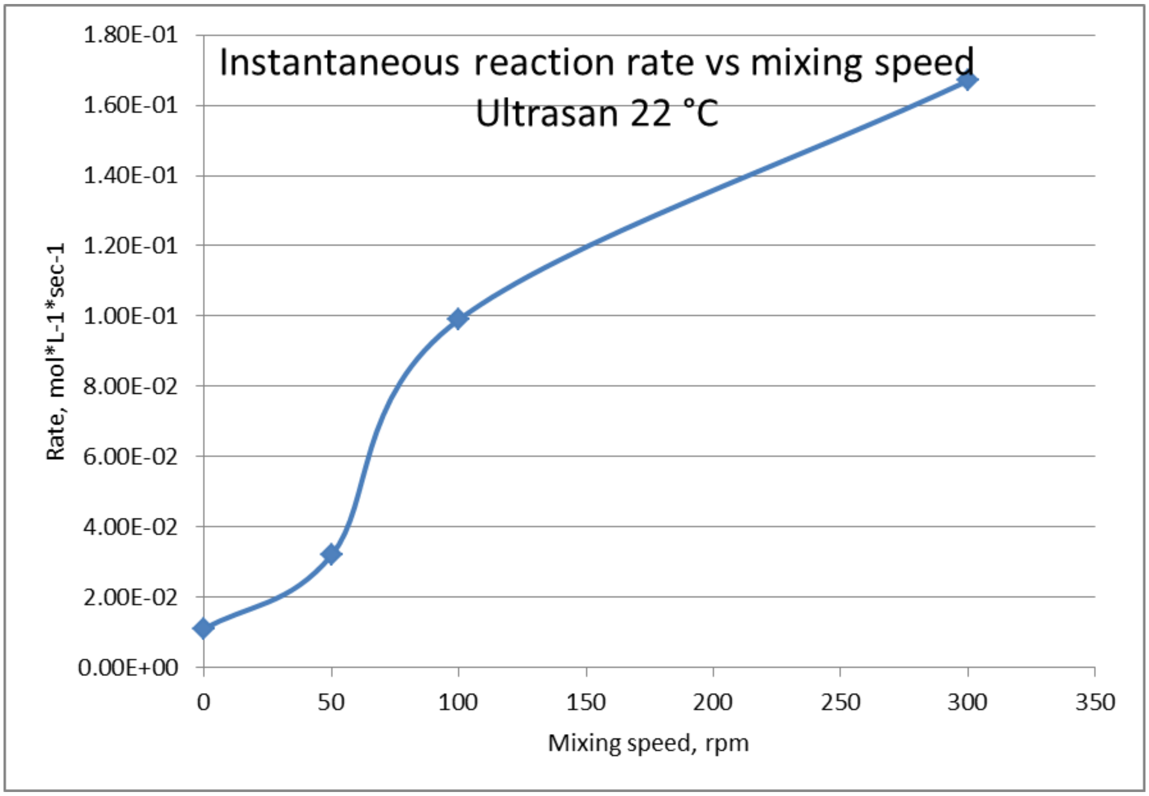


Fig. 96 Instantaneous (max) reaction rate vs. mixing speed for Ultrasan at 22 °C

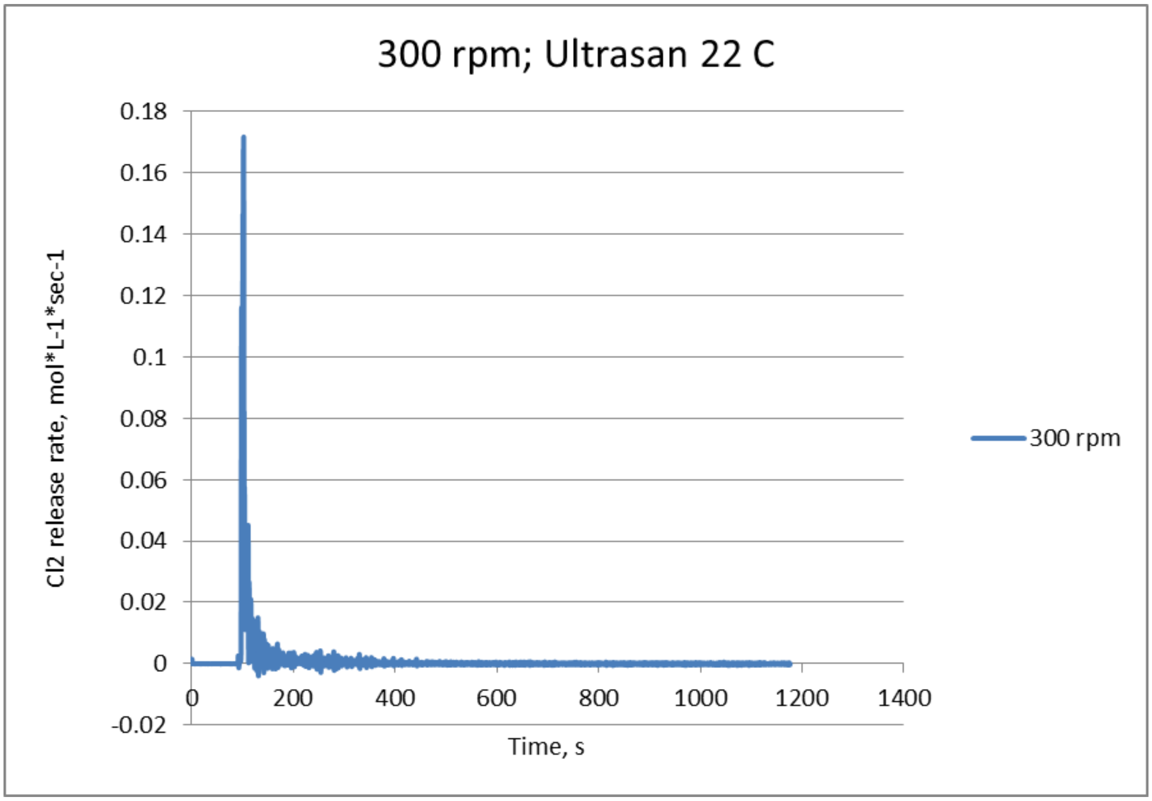


Fig. 97 Instantaneous reaction rate vs. time for Ultrasan at 22 °C at 300 rpm mixing speed

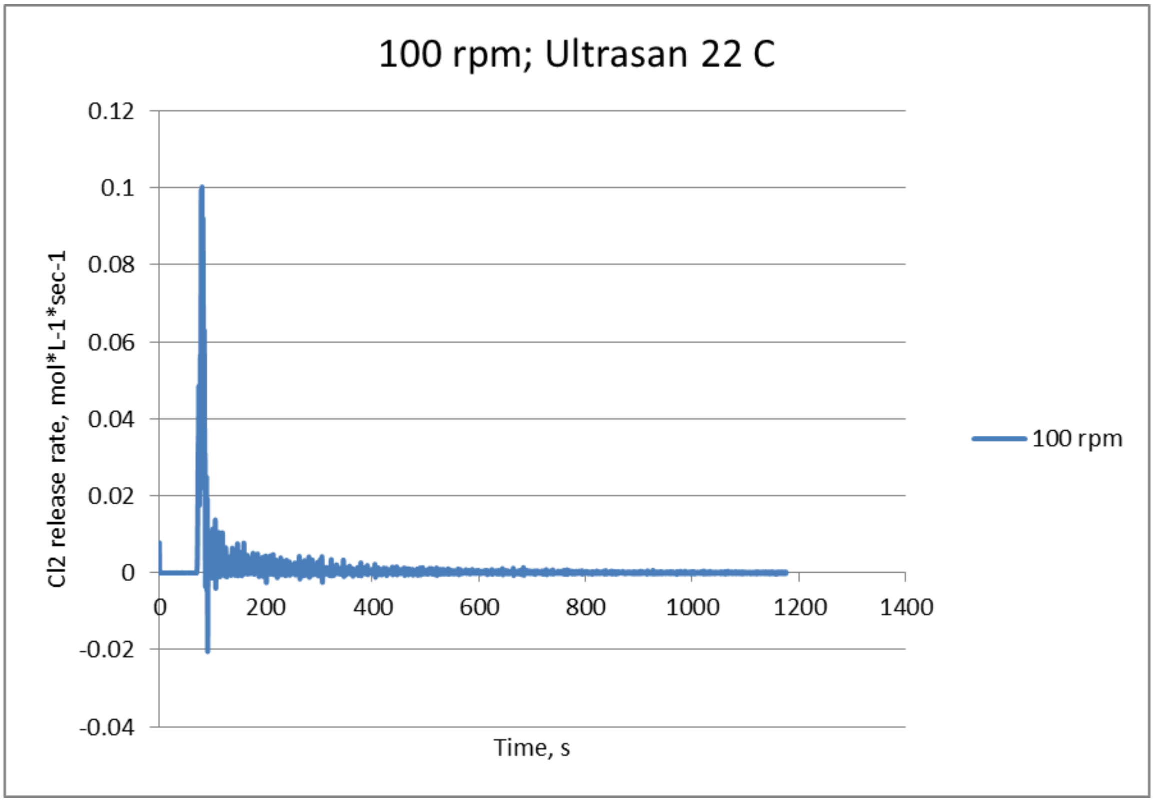


Fig. 98 Instantaneous reaction rate vs. time for Ultrasan at 22 °C at 100 rpm mixing speed

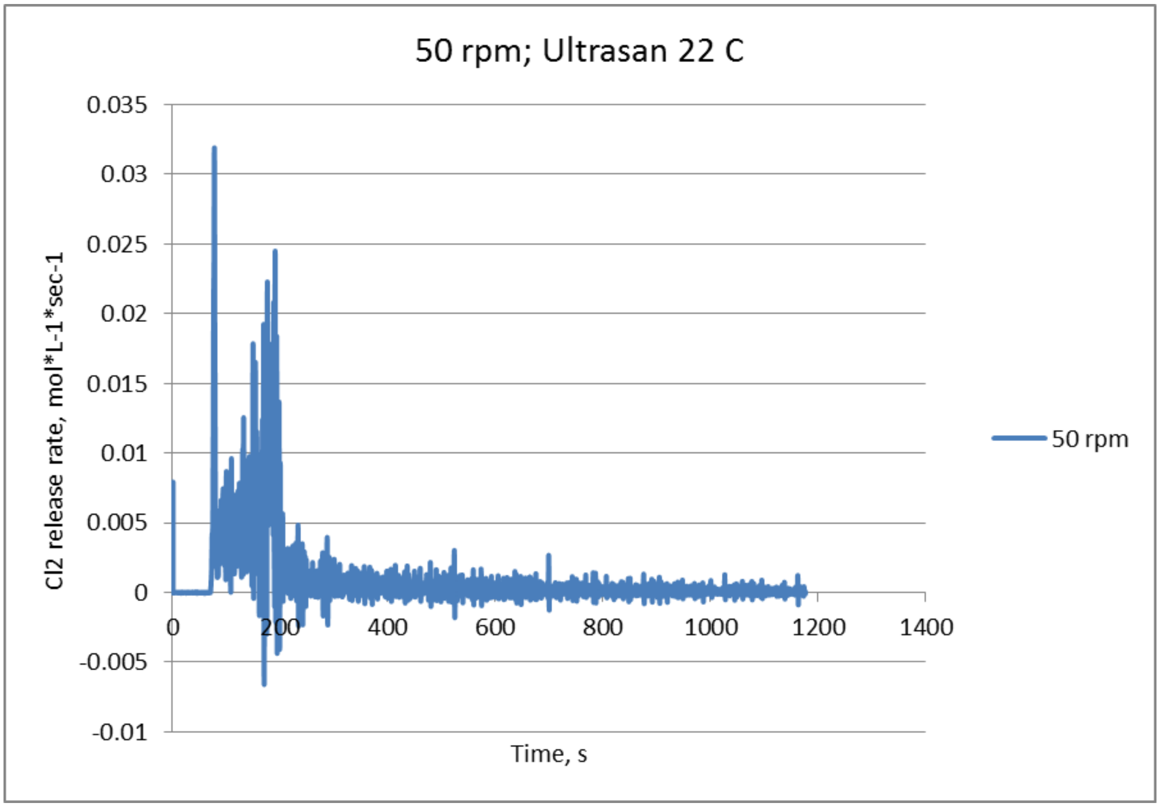


Fig. 99 Instantaneous reaction rate vs. time for Ultrasan at 22 °C at 50 rpm mixing speed

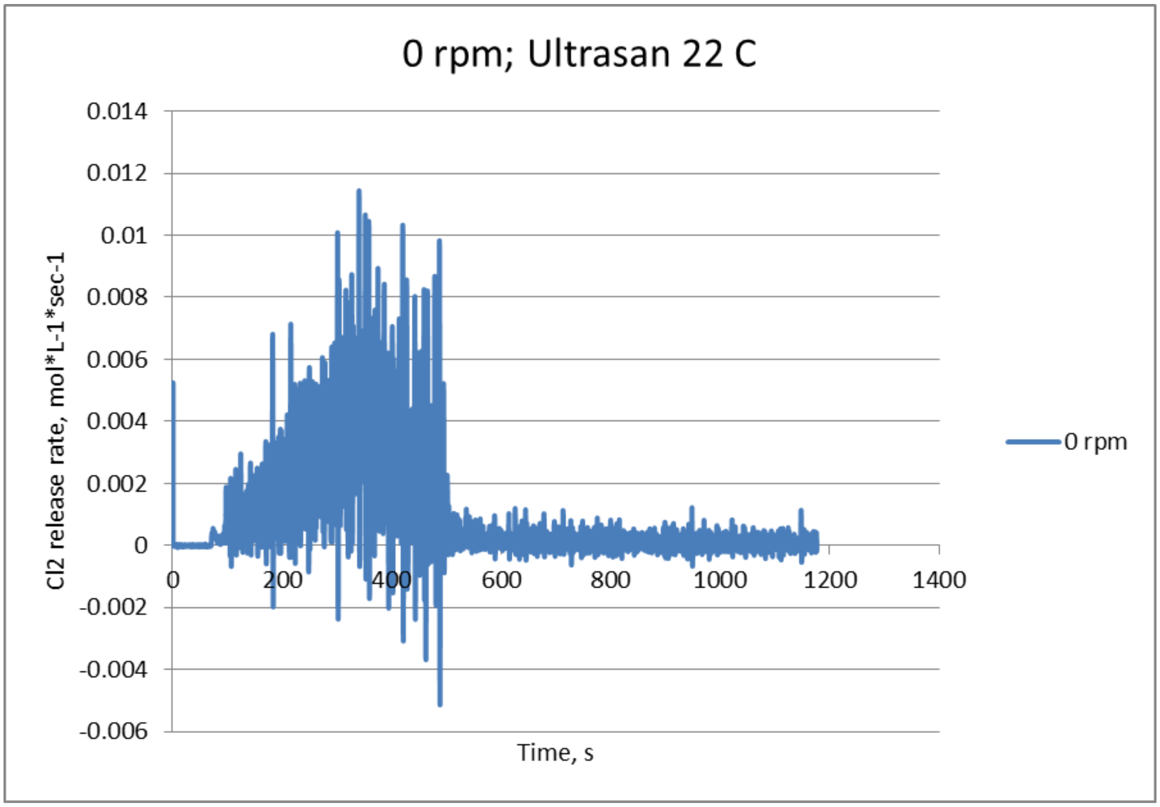


Fig. 100 . Instantaneous reaction rate vs. time for Ultrasan at 22 °C at 0 rpm mixing speed

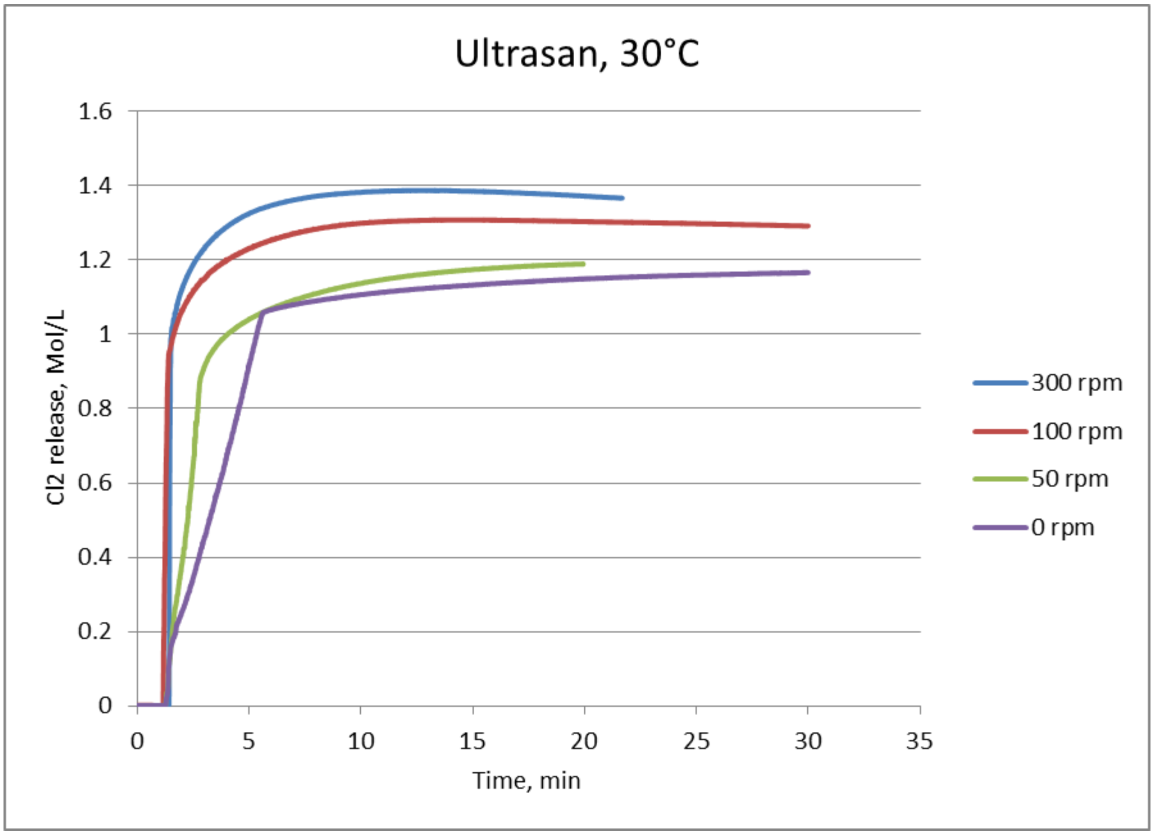


Fig. 101 Chlorine release from Ultrasan product reacted with HCl at 30 °C and different mixing speeds

Table 31. Initial and instantaneous maximal point rates of chlorine release from Ultrasan product at 30 °C:

Initial

Speed	Rate
0	3.52E-03
50	8.87E-03
100	6.90E-02
300	1.52E-01

instantaneous

Speed	Rate
0	3.70E-02
50	4.80E-02
100	1.31E-01
300	4.65E-01

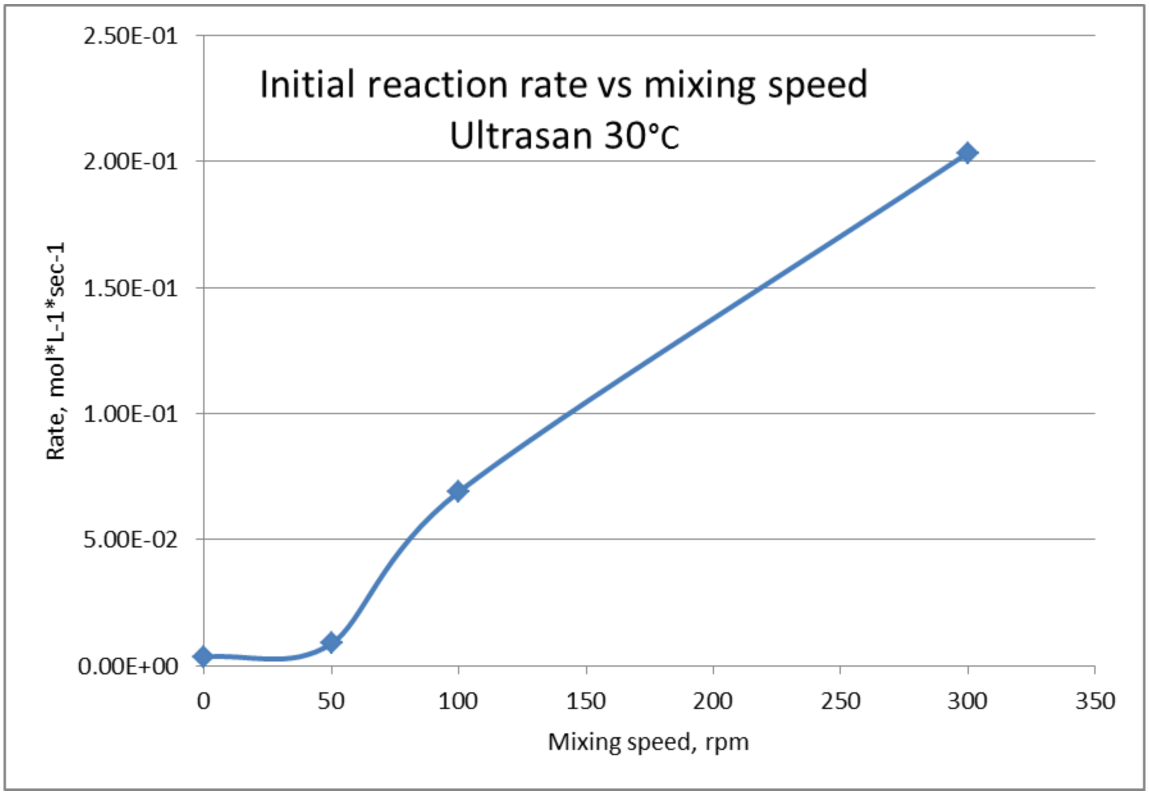


Fig. 102 Initial reaction rate vs. mixing speed for Ultrasan at 30 °C

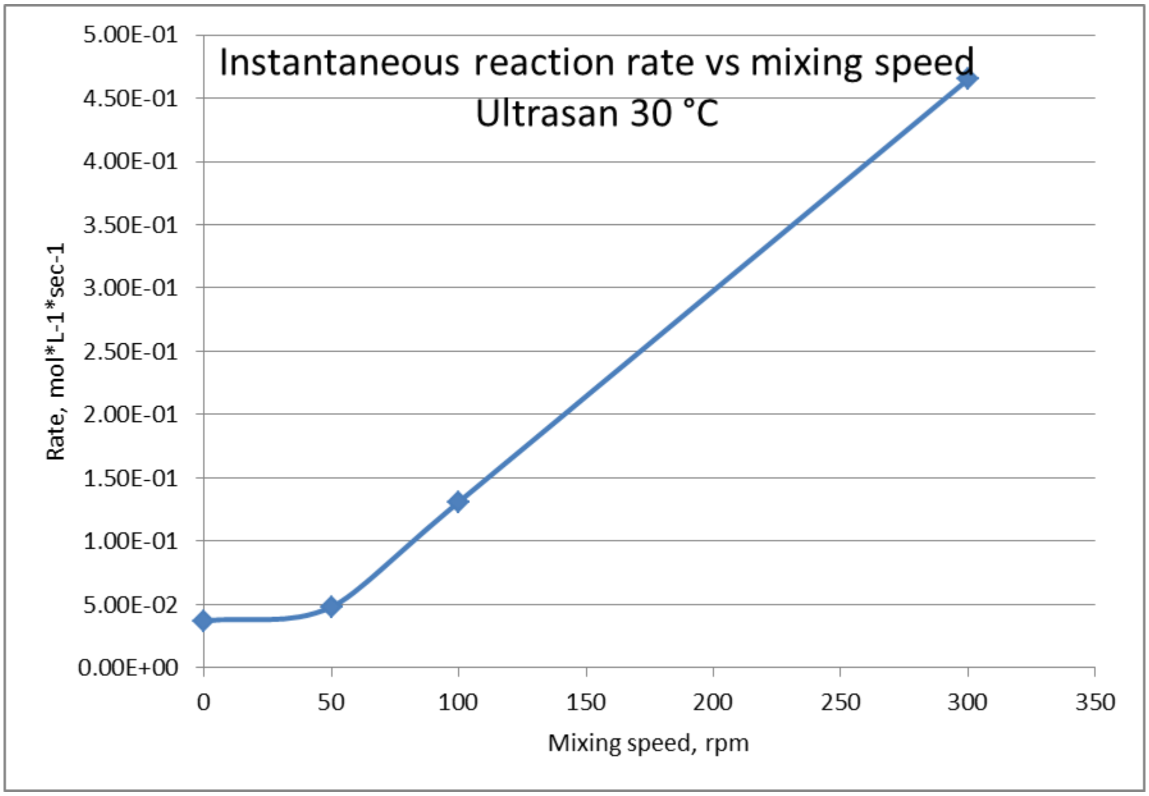


Fig. 103 Instantaneous (maximal point) reaction rate vs. mixing speed for Ultrasan at 30 °C

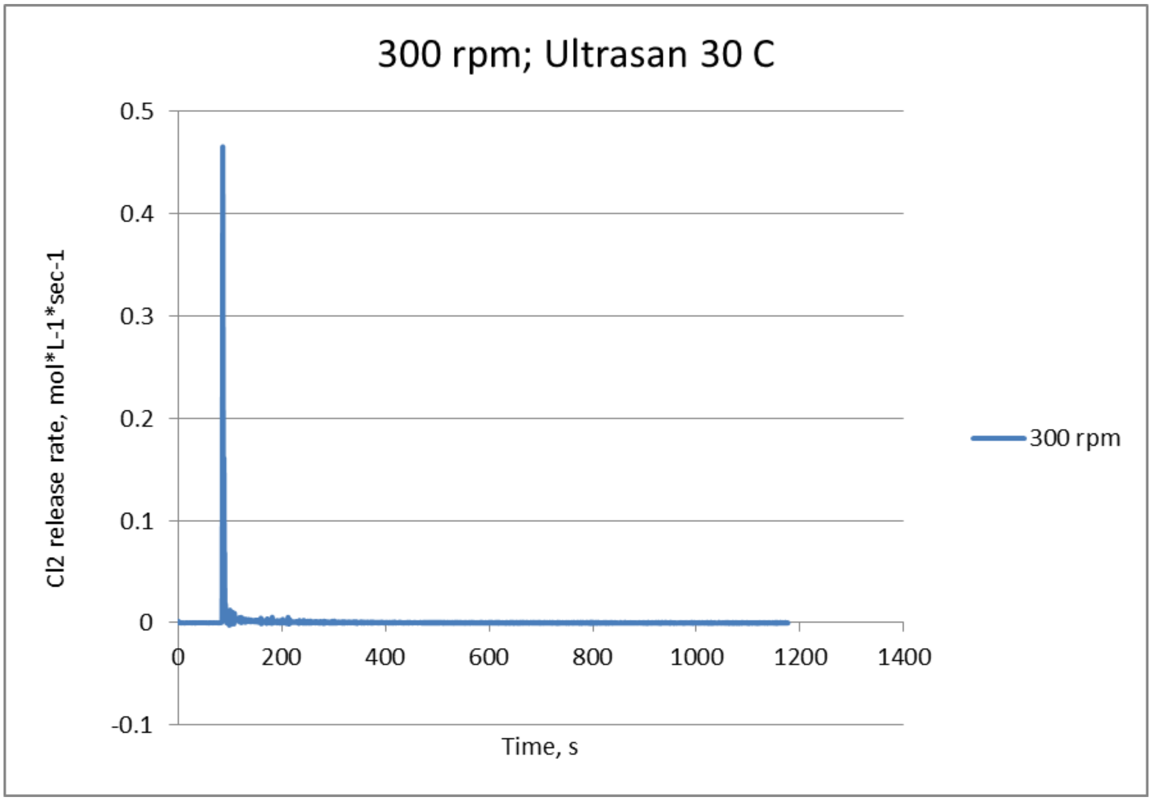


Fig. 104 Instantaneous reaction rate vs. time for Ultrasan at 30 °C at 300 rpm mixing speed

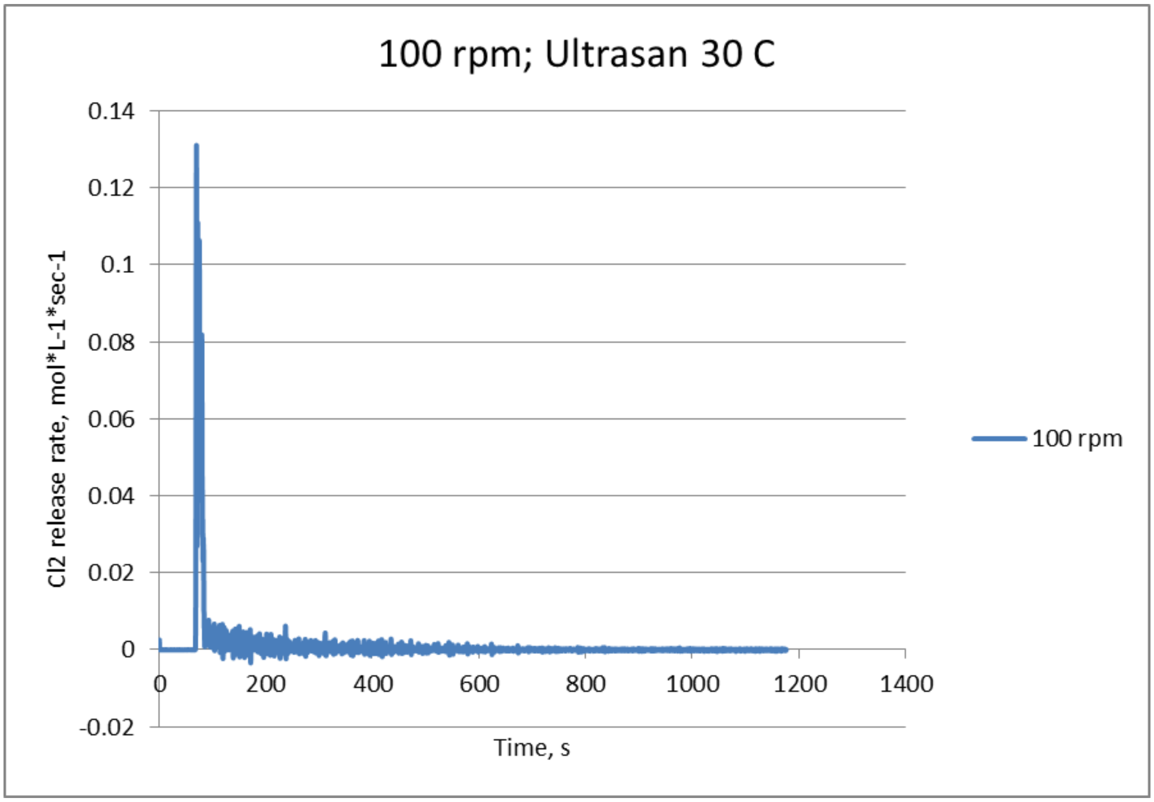


Fig. 105 Instantaneous reaction rate vs. time for Ultrasan at 30 °C at 100 rpm mixing speed

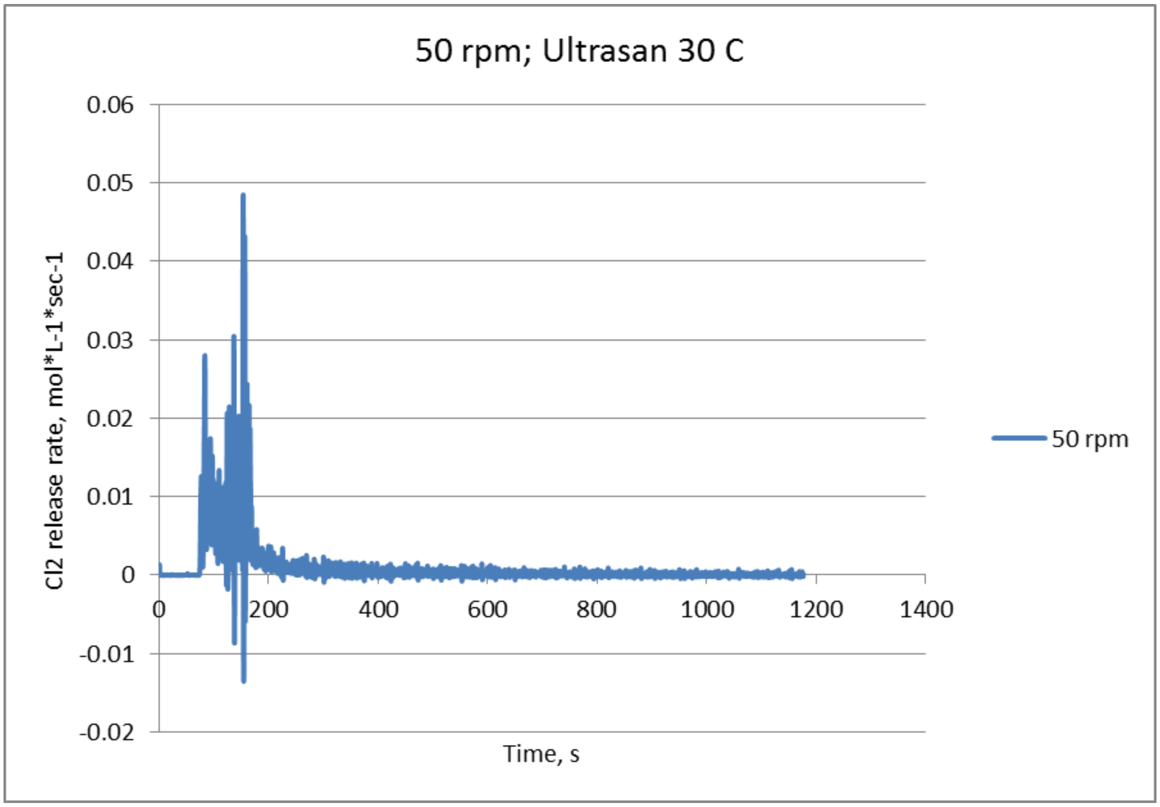


Fig. 106 Instantaneous reaction rate vs. time for Ultrasan at 30 °C at 50 rpm mixing speed

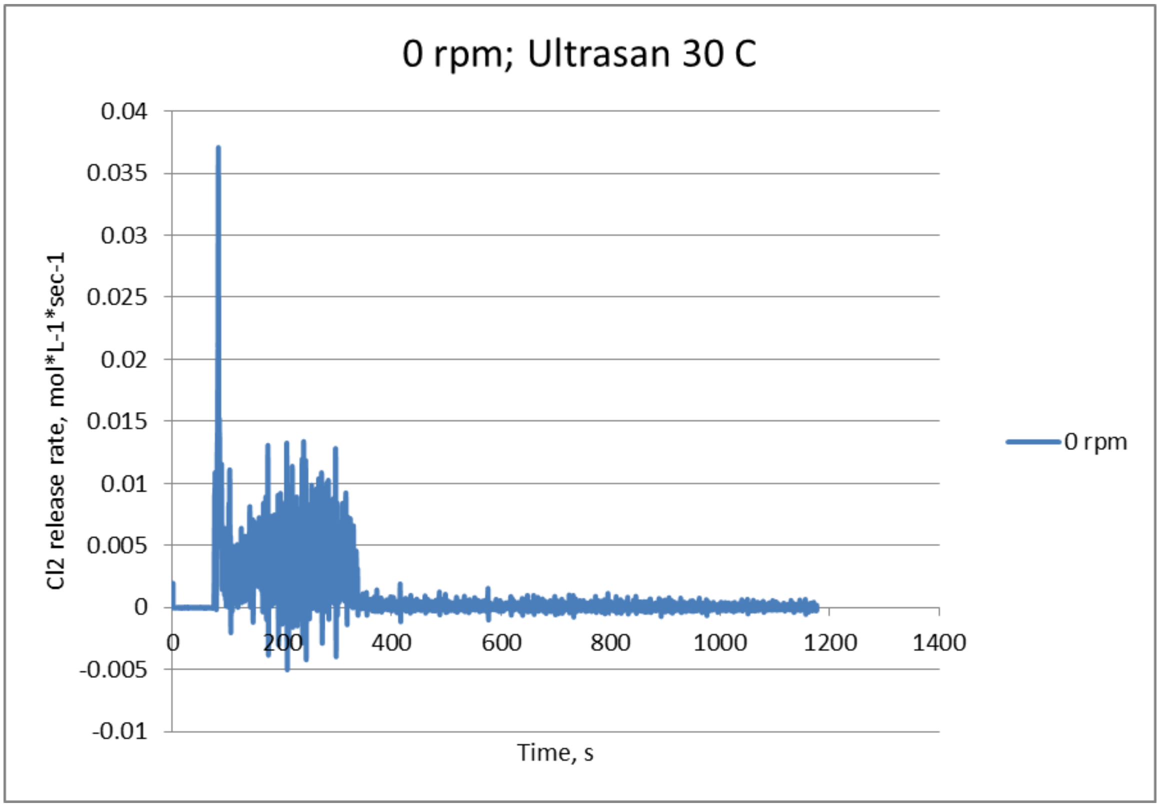


Fig. 107 Instantaneous reaction rate vs. time for Ultrasan at 30 °C at 0 rpm mixing speed

4.4.2.1. Arrhenius Parameters for Ultra san:

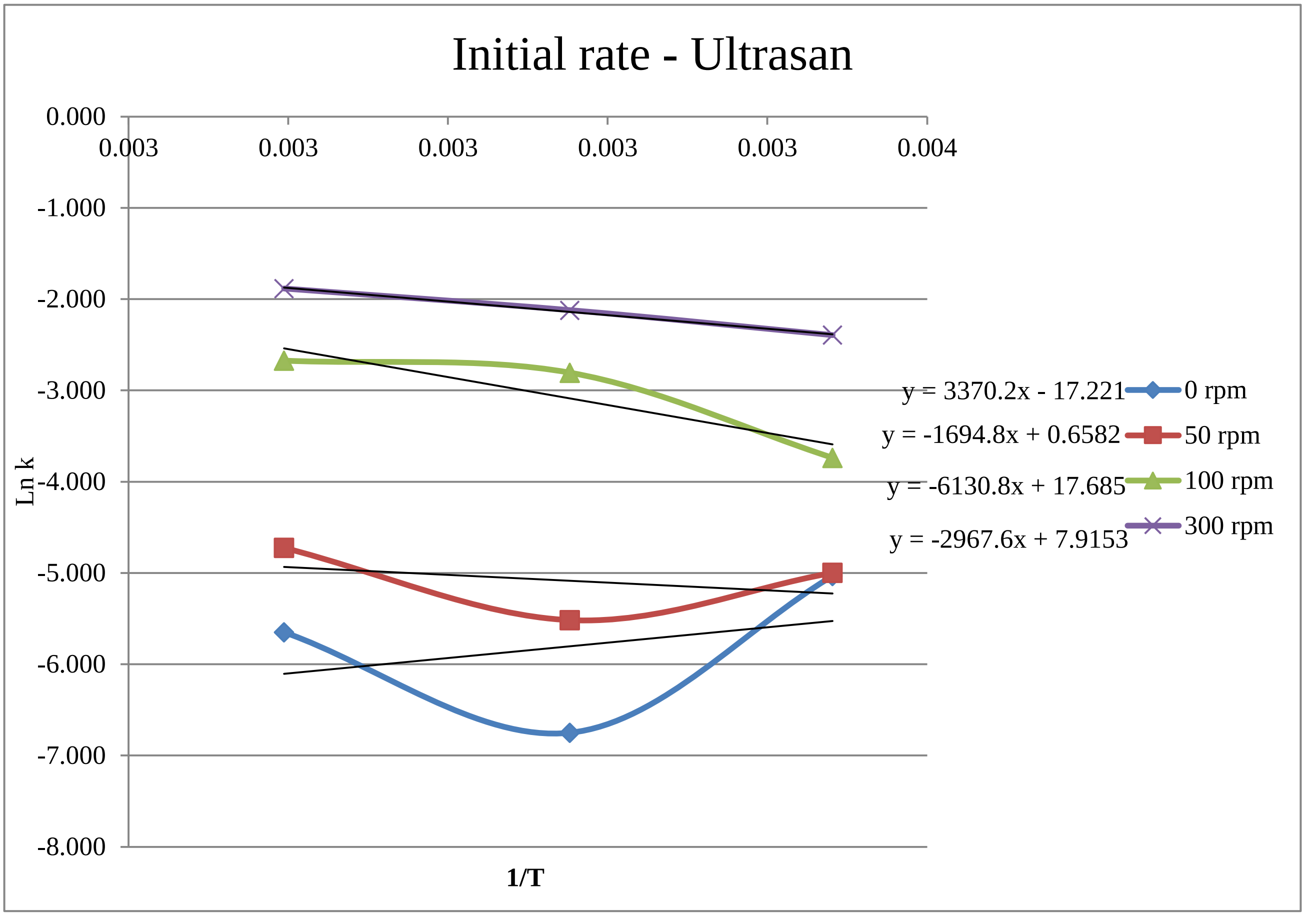


Fig. 108 Arrhenius plots for Ultrasan – initial rate

Table 32. Initial rate kinetic parameters for Ultrasan:

Initial k

t	0 rpm	50 rpm	100 rpm	300 rpm
15	6.53E-03	6.75E-03	2.38E-02	9.13E-02
22	1.17E-03	4.02E-03	6.05E-02	1.20E-01
30	3.52E-03	8.87E-03	6.90E-02	0.1521

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.003	-5.031	-4.998	-3.738	-2.394
0.003	-6.751	-5.516	-2.805	-2.120
0.003	-5.649	-4.725	-2.674	-1.883
M =	3370.200	-1694.800	-6130.800	-2967.600
B =	-17.221	0.658	17.685	7.915
E_a =	-28.020	14.091	50.971	24.673
A=	3.319E-08	1.931E+00	4.792E+07	2.739E+03

The negative energy of activation means that the reaction is controlled by diffusion and mixing at low mixing speeds, but not by thermodynamics.

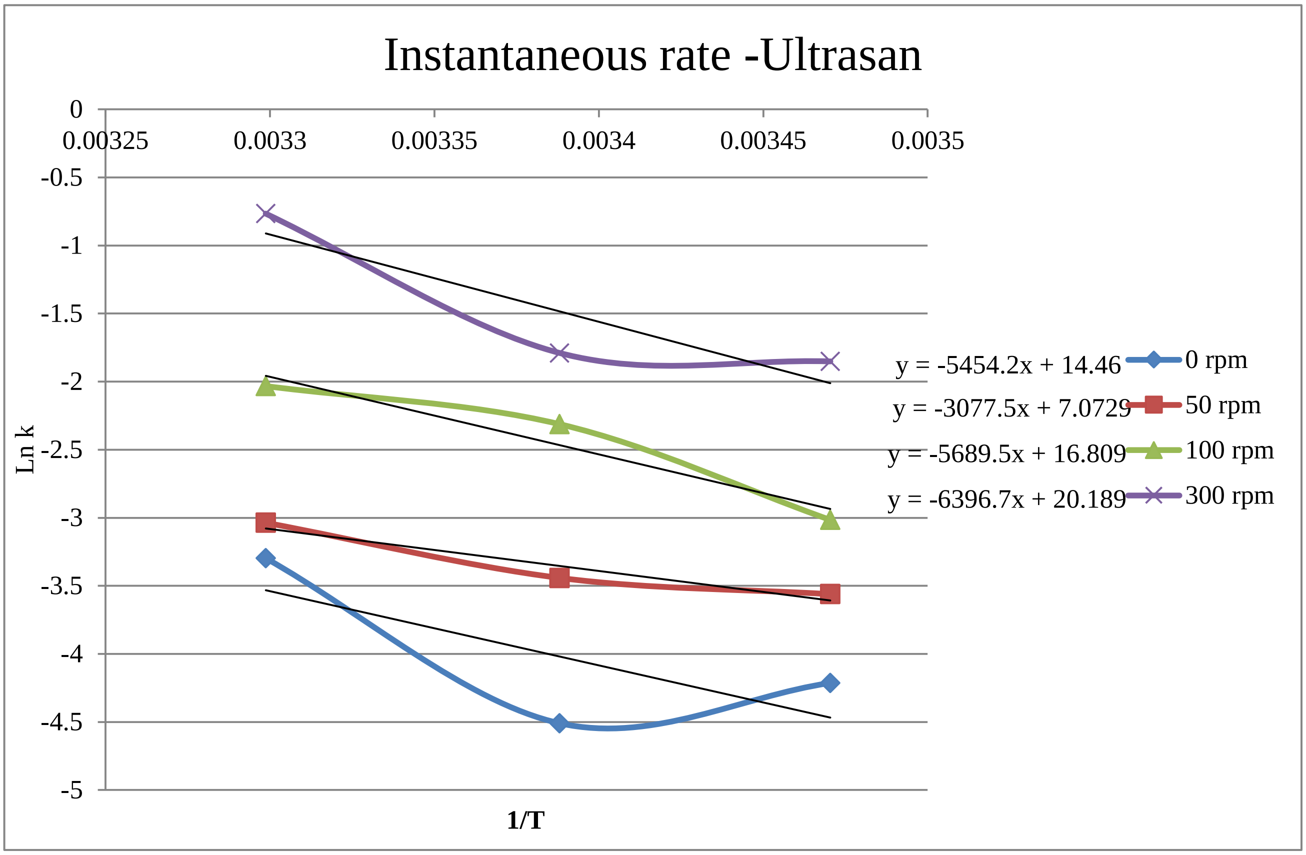


Fig. 109 Arrhenius plots for Ultrasan – instantaneous maximal point rate

Table 33. Instantaneous rate kinetic parameters for Ultrasan:

Instant

t, C	0 rpm	50 rpm	100 rpm	300 rpm
15	1.48E-02	2.84E-02	4.90E-02	1.57E-01
22	1.10E-02	3.20E-02	9.90E-02	1.67E-01
30	3.70E-02	4.80E-02	1.31E-01	4.65E-01

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.0035	-4.2131	-3.5614	-3.0159	-1.8515
0.0034	-4.5099	-3.4420	-2.3126	-1.7898
0.0033	-3.2968	-3.0366	-2.0326	-0.7657
M =	-5454.2	-3077.5	-5689.5	-6396.7
B =	14.46	7.0729	16.8	20.18
E_a =	45.346	25.586	47.303	53.182
A=	1.905E+06	1.180E+03	1.978E+07	5.808E+08

4.4.3. Liquid Plumr

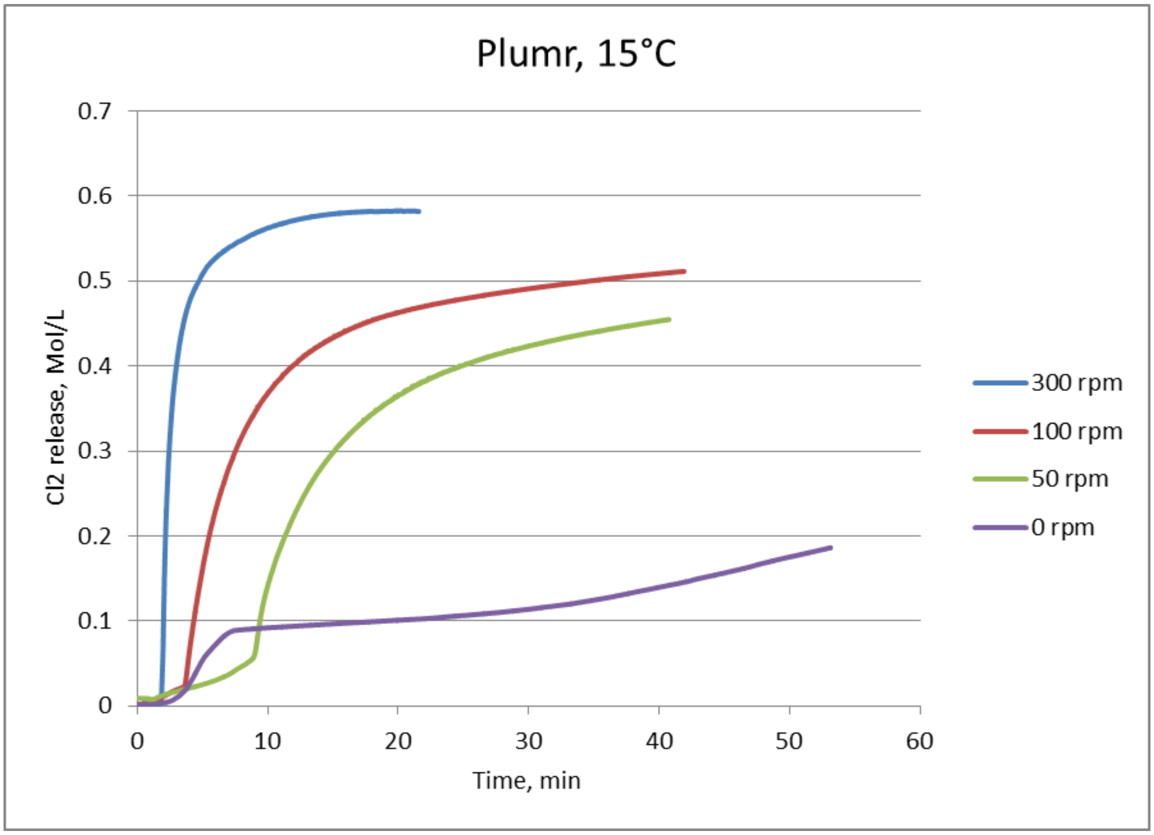


Fig. 110 Chlorine release from Plumr product reacted with HCl at 15 °C and different mixing speeds

Table 34. Initial and instantaneous maximal point rates of chlorine release from Plumr product at 15 °C

Initial

Speed	Rate
0	4.12E-04
50	8.08E-04
100	1.60E-03
300	1.02E-02

instantaneous

Speed	Rate
0	6.70E-04
50	2.00E-03
100	2.98E-03
300	1.58E-02

This product exhibited the most dramatic dependence of chlorine release rate on the mixing speed. The explanation is that, at a mixing speed of zero, the very high viscosity of Liquid Plumr resulted in only 1/3 of the product being mixed with acid during the entire time of the experiment.

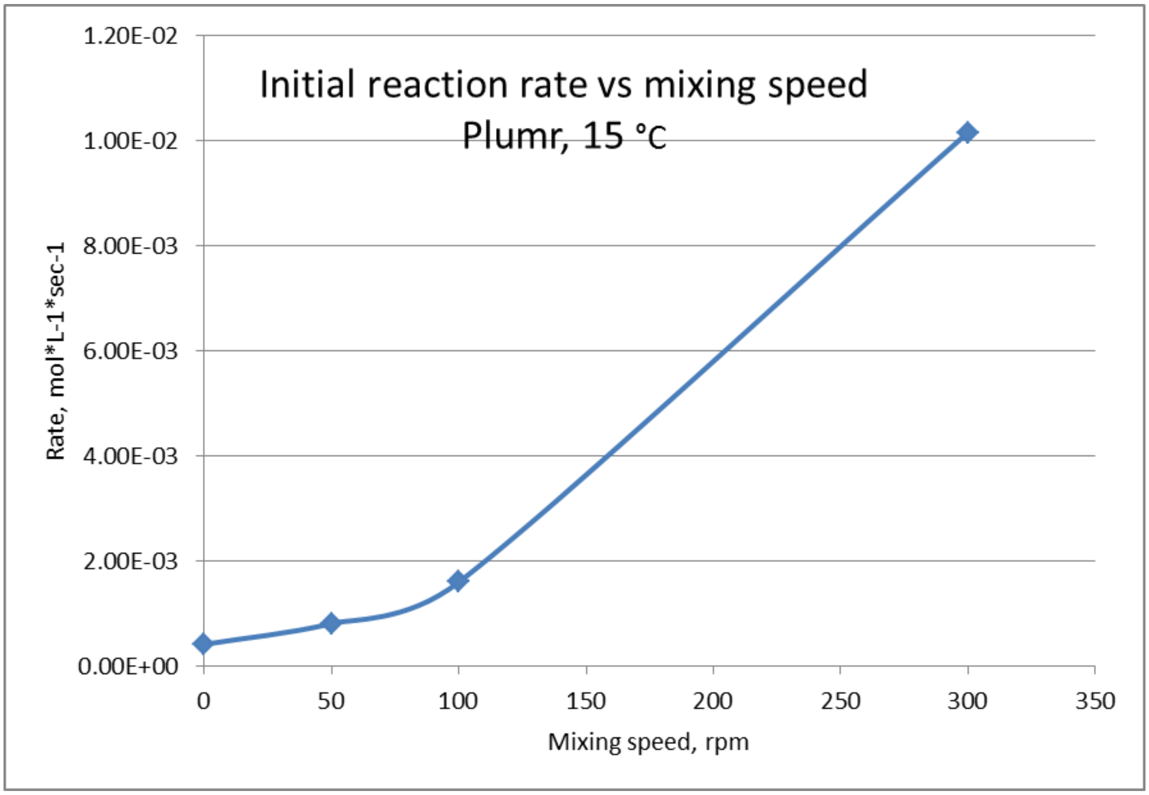


Fig. 111 Initial reaction rate vs. mixing speed for Plumr at 15 °C

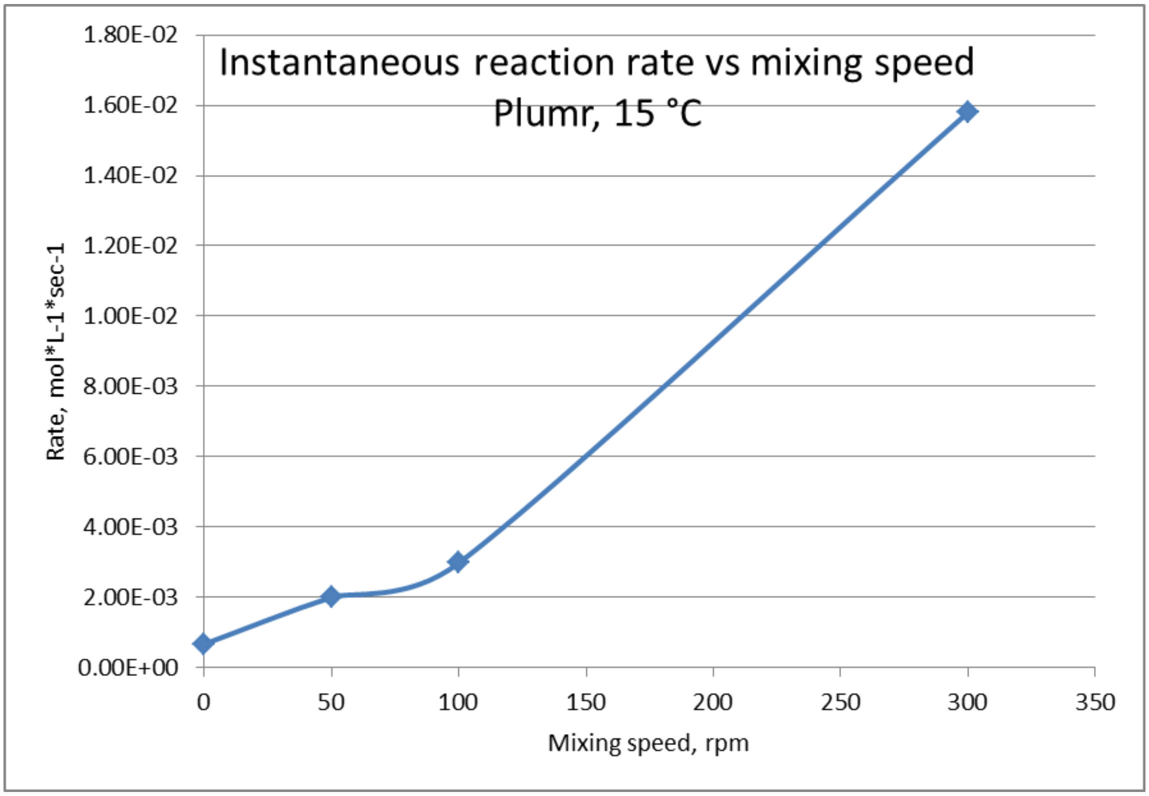


Fig. 112 Instantaneous (maximal point) reaction rate vs. mixing speed for Plumr at 15 °C

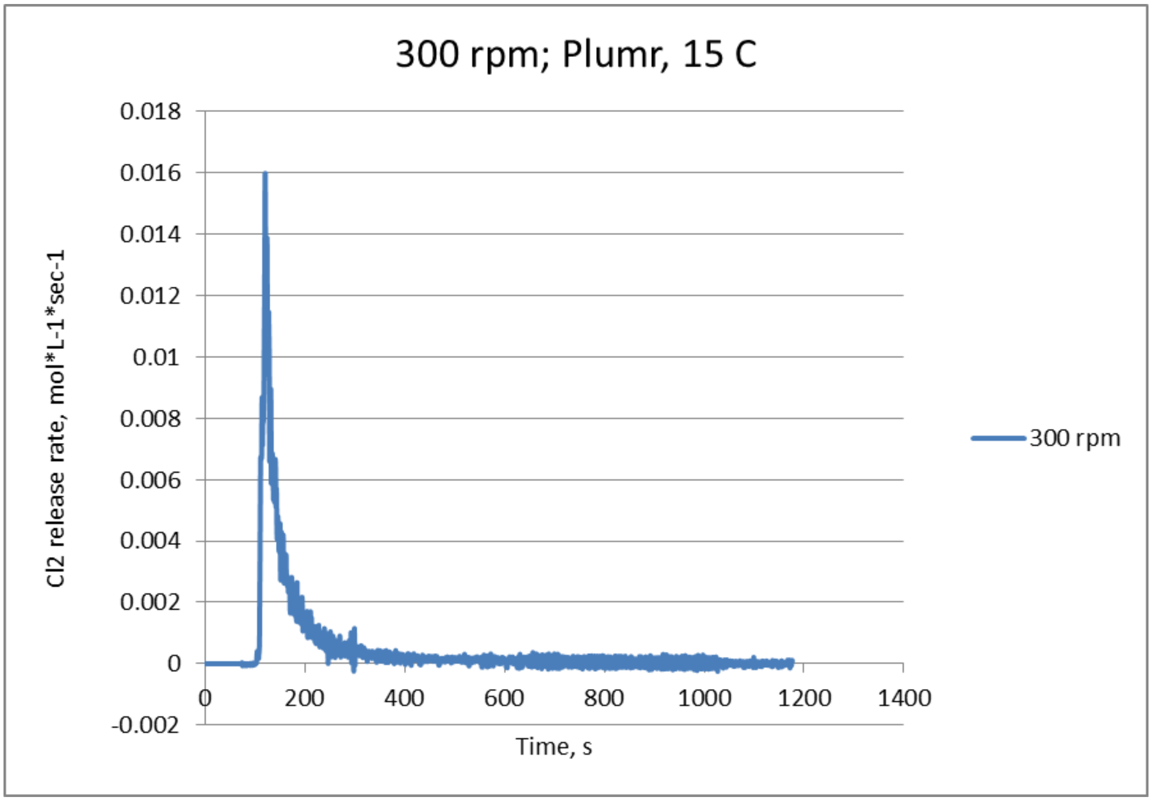


Fig. 113 Instantaneous reaction rate vs. time for Plumr at 15 °C at 300 rpm mixing speed

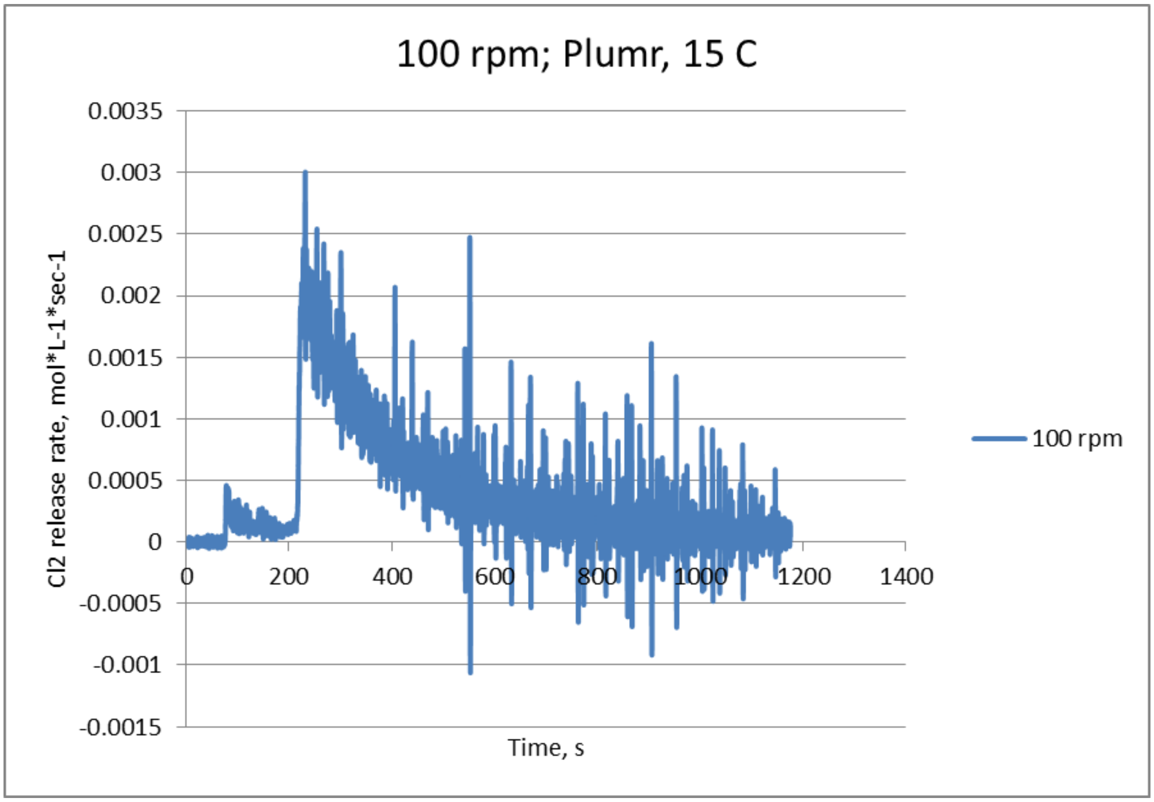


Fig. 114 Instantaneous reaction rate vs. time for Plumr at 15 °C at 100 rpm mixing speed

The product Liquid Plumr has some surfactants and soluble polymers as thickening agents. As a result, large chlorine bubbles are formed and they appear as positive and negative peaks on the rate plot.

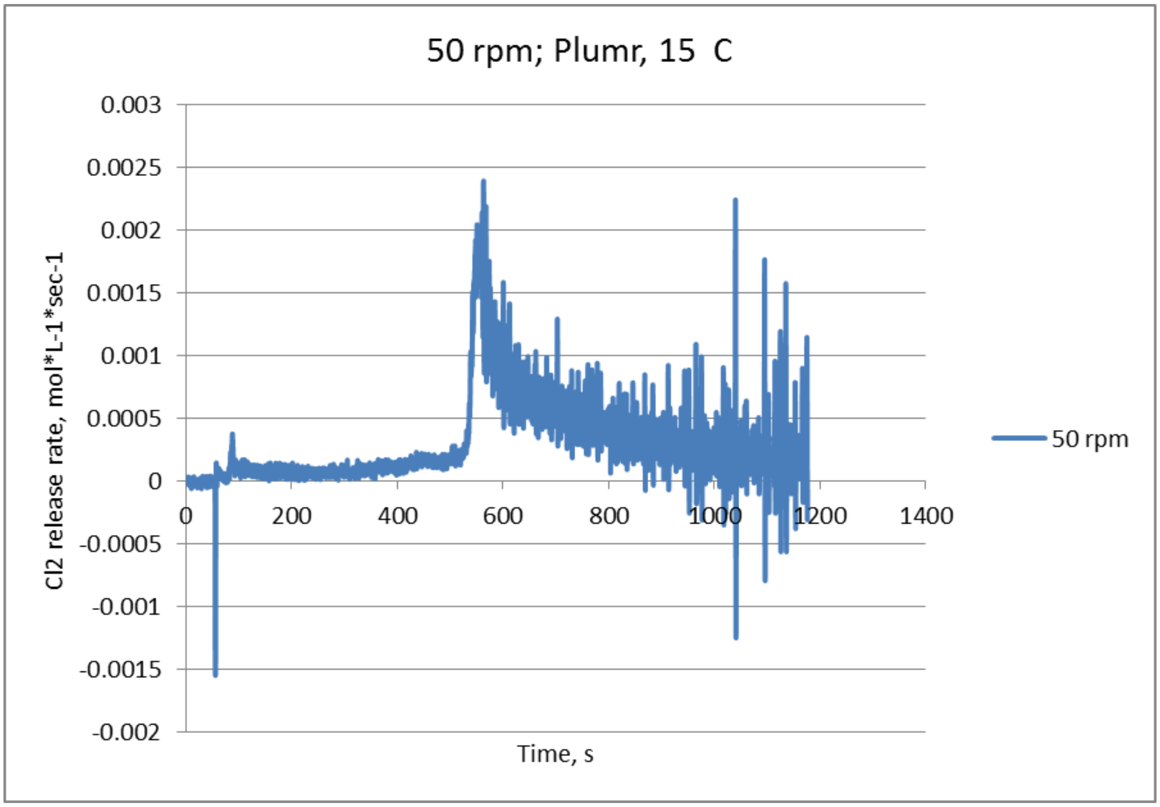


Fig. 115 . Instantaneous reaction rate vs. time for Plumr at 15 °C at 50 rpm mixing speed

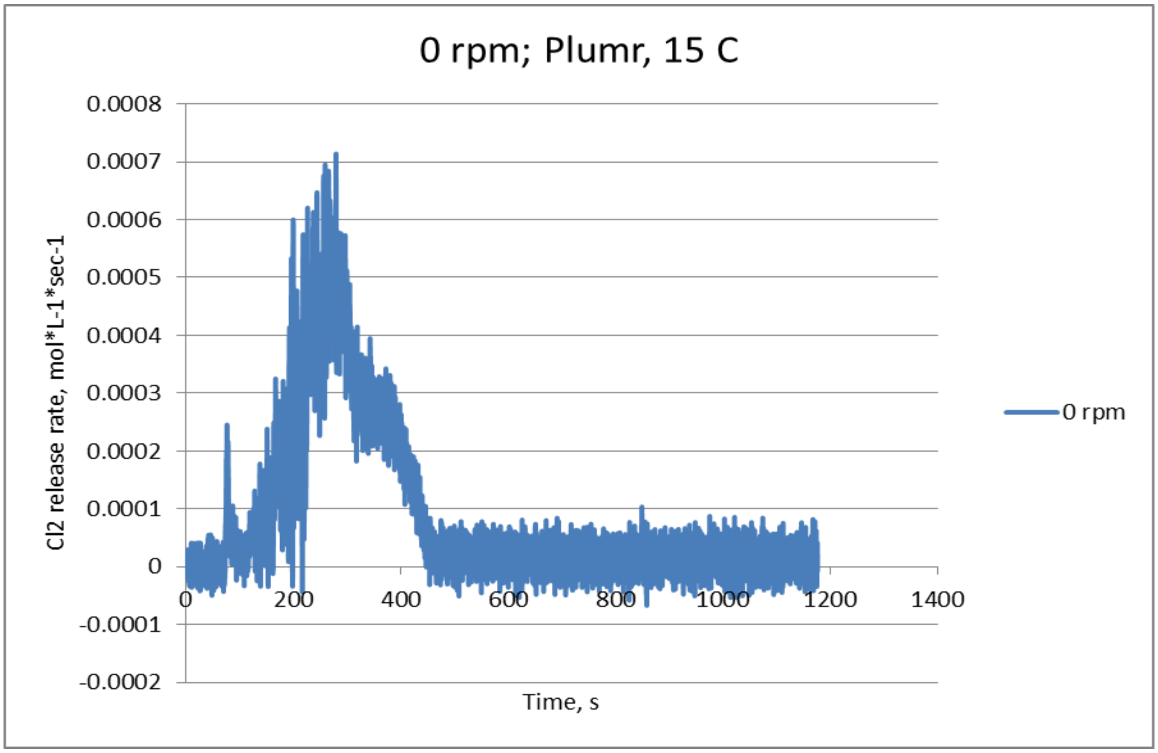


Fig. 116. Instantaneous reaction rate vs. time for Plumr at 15 °C at 0 rpm mixing speed

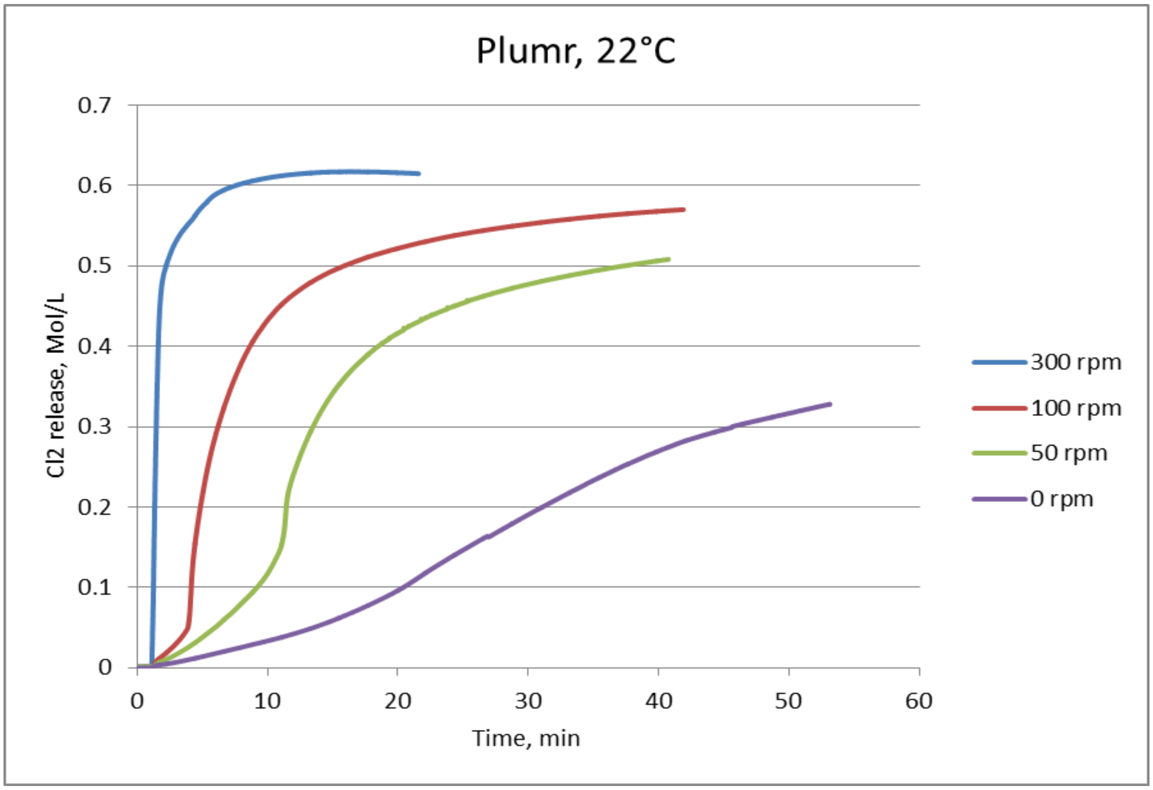


Fig. 117. Chlorine release from Plumr product reacted with HCl at 22 °C and different mixing speeds

Table 35. Initial and instantaneous maximal point rates of chlorine release from Plumr product at 22 °C:

Initial

Speed	Rate
0	6.50E-05
50	4.93E-04
100	2.20E-03
300	1.28E-02

Instantaneous

Speed	Rate
0	3.30E-04
50	3.85E-03
100	5.53E-03
300	1.96E-02

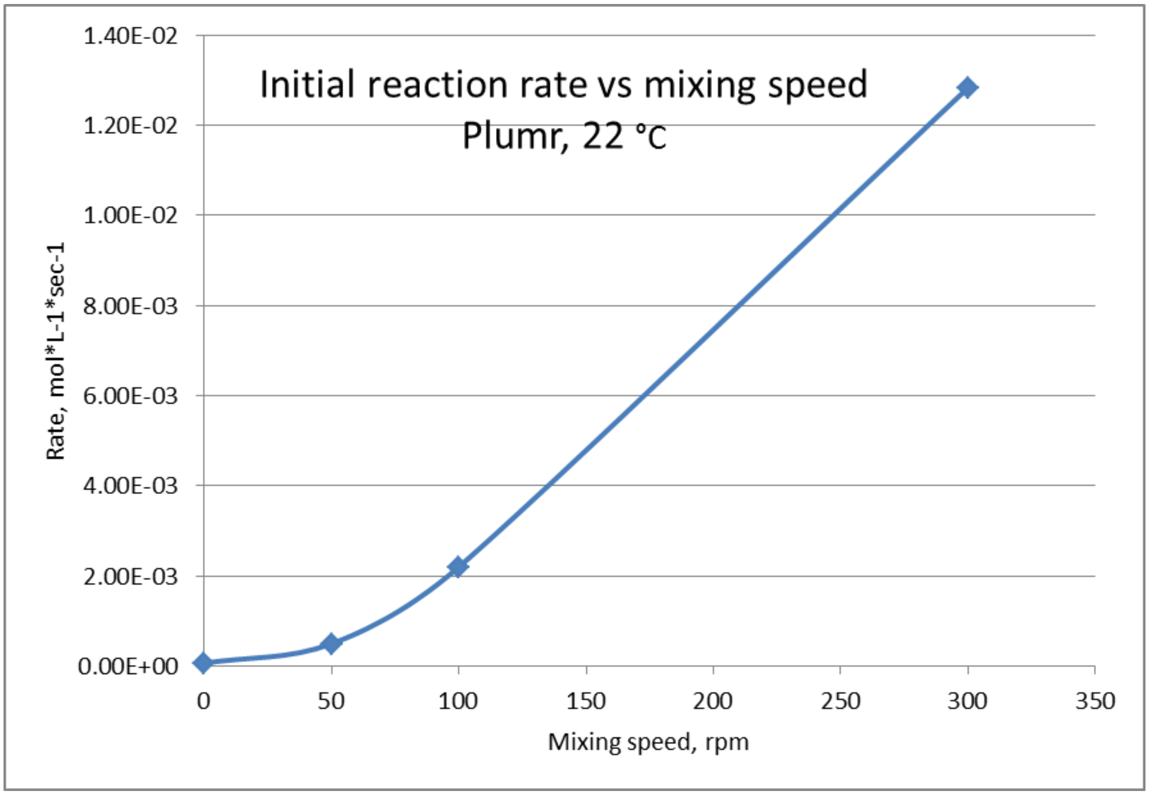


Fig. 118 Initial reaction rate vs. mixing speed for Plumr at 22 °C

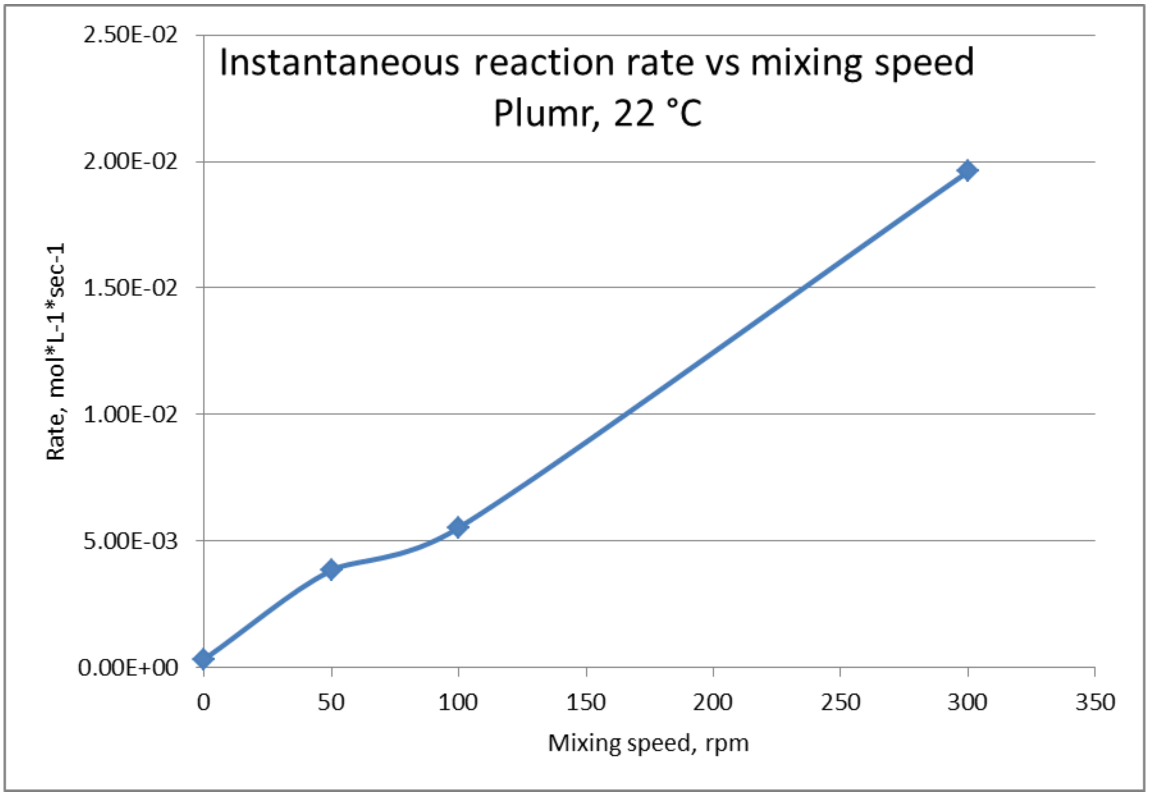


Fig. 119 Instantaneous (maximal point) reaction rate vs. mixing speed for Plumr at 22 °C

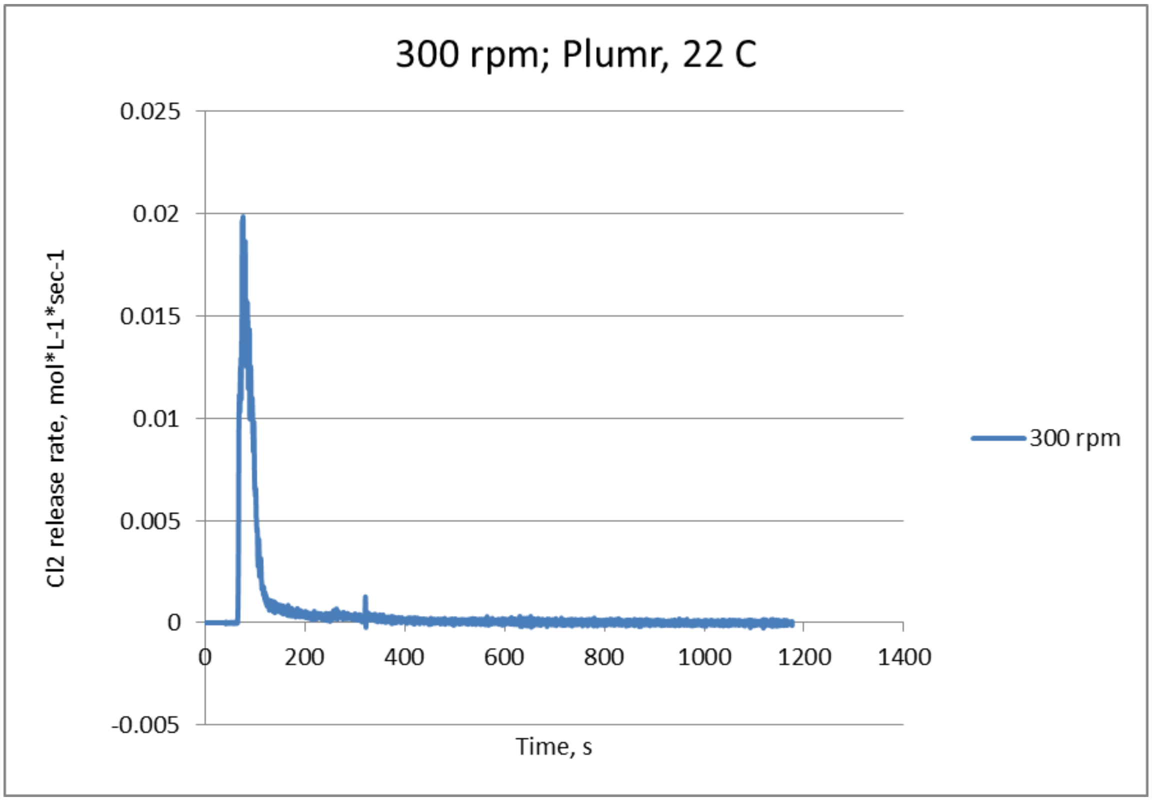


Fig. 120 Instantaneous reaction rate vs. time for Plumr at 22 °C at 300 rpm mixing speed

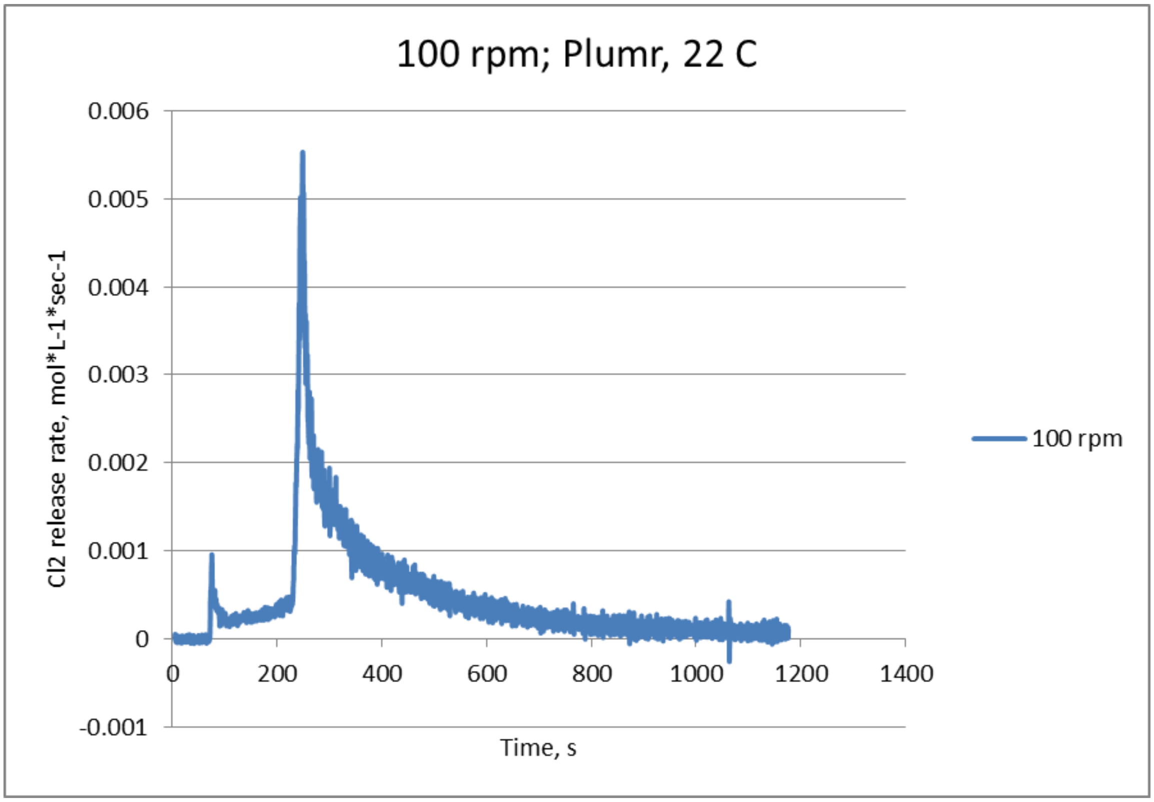


Fig. 121 Instantaneous reaction rate vs. time for Plumr at 22 °C at 100 rpm mixing speed

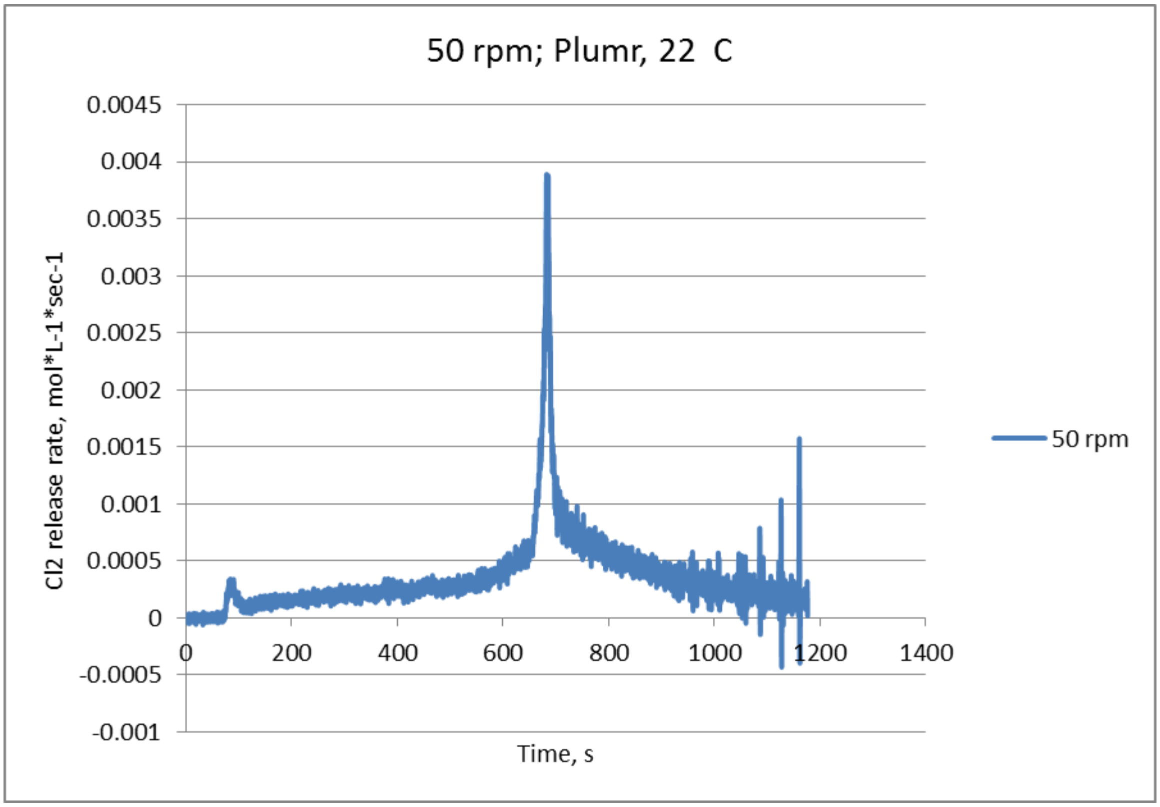


Fig. 122 Instantaneous reaction rate vs. time for Plumr at 22 °C at 50 rpm mixing speed

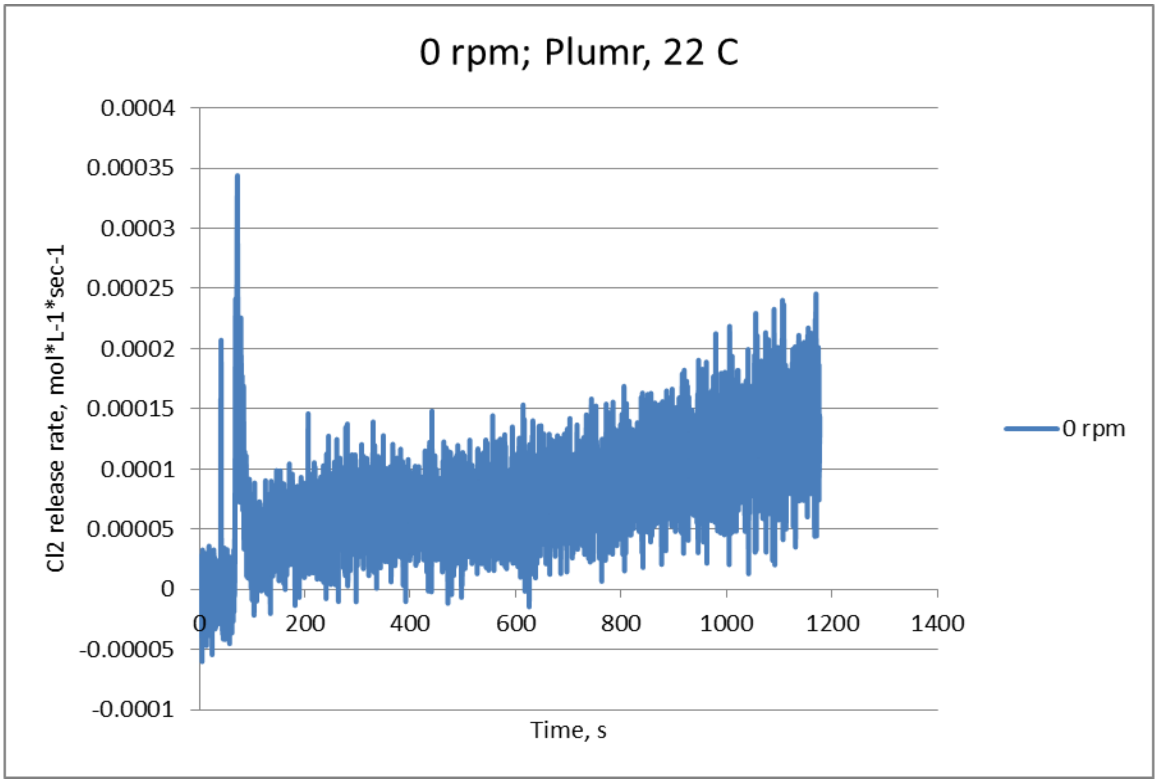


Fig. 123 Instantaneous reaction rate vs. time for Plumr at 22 °C at 0 rpm mixing speed

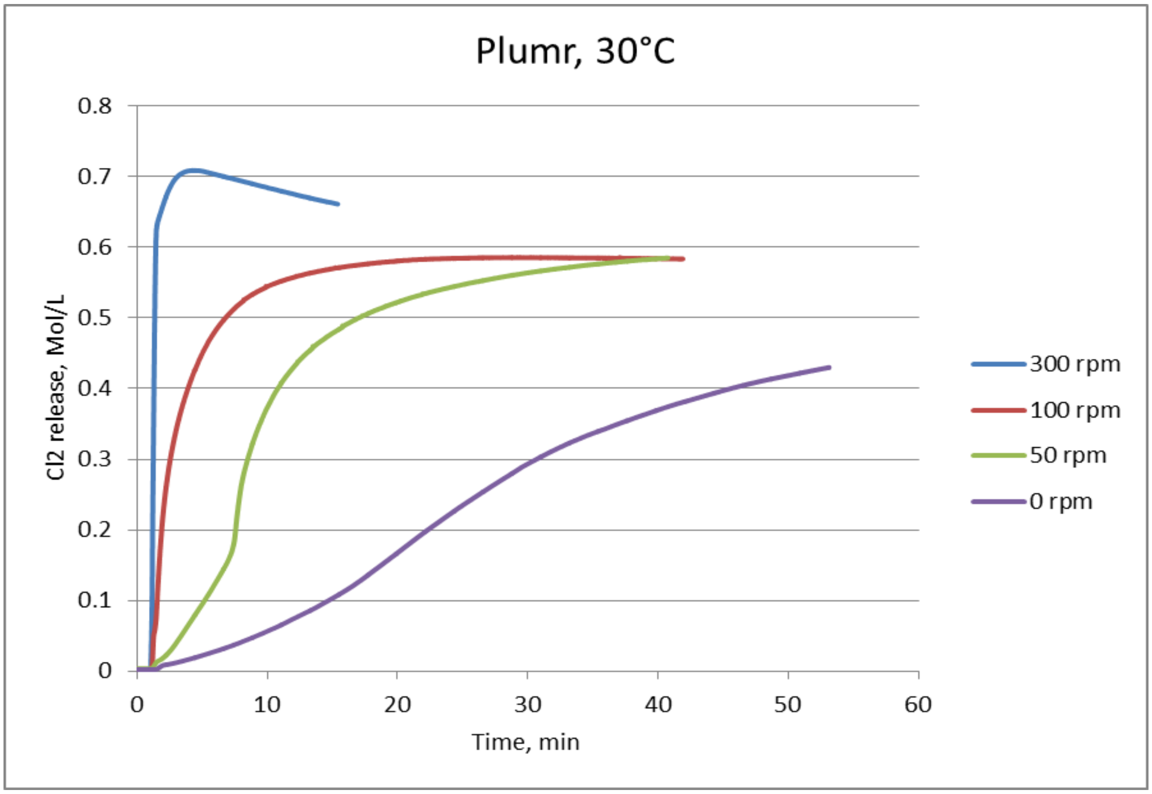


Fig. 124 Chlorine release from Plumr product reacted with HCl at 30 °C and different mixing speeds

Table 36. Initial and instantaneous maximal point rates of chlorine release from Plumr product at 30 °C:

Initial

Speed	Rate
0	1.19E-04
50	4.68E-04
100	4.50E-03
300	2.33E-02

Instantaneous

Speed	Rate
0	3.00E-04
50	3.50E-03
100	8.50E-03
300	4.80E-02

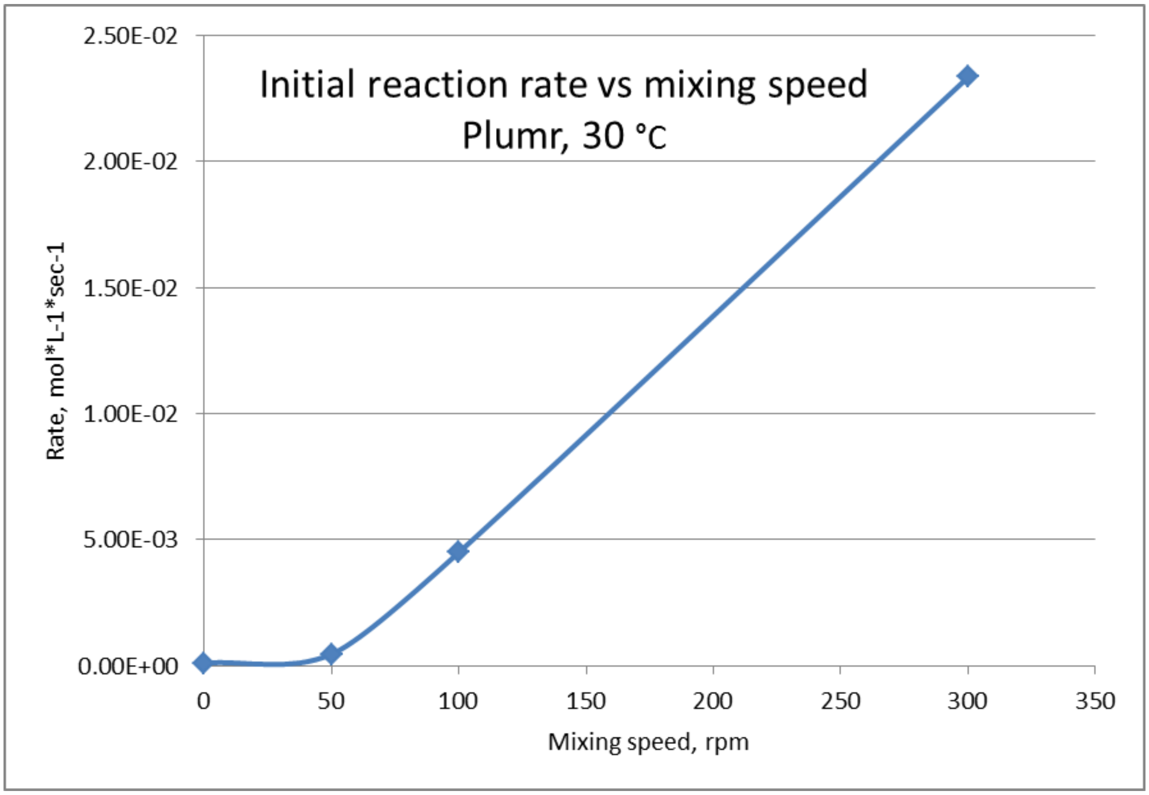


Fig. 125 Initial reaction rate vs.. mixing speed for Plumr at 30 °C

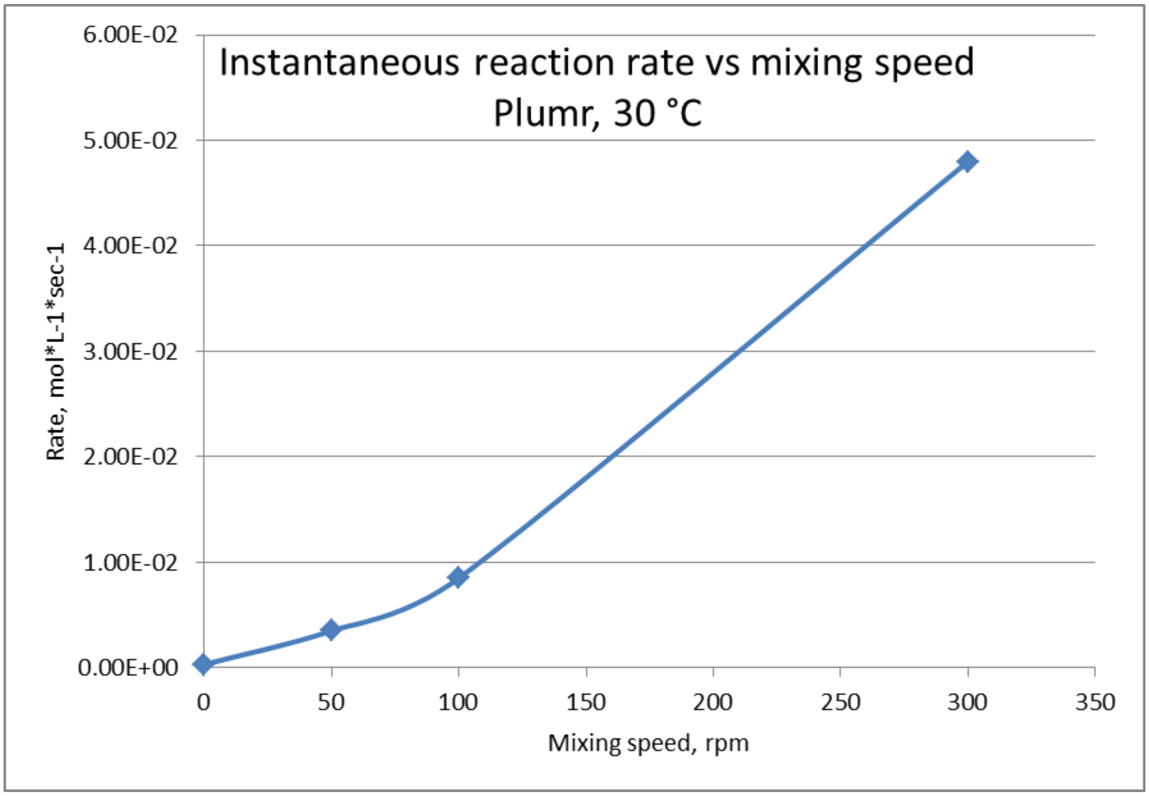


Fig. 126 Instantaneous (maximal point) reaction rate vs.. mixing speed for Plumr at 30 °C

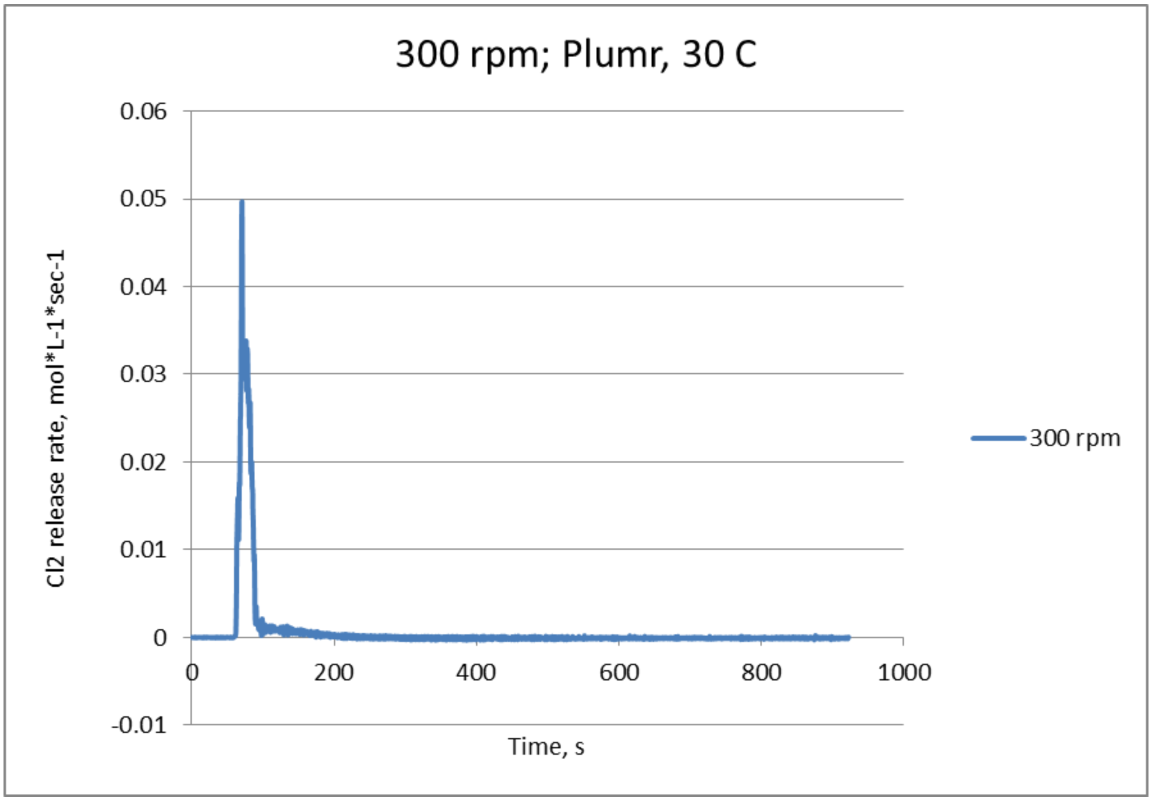


Fig. 127 Instantaneous reaction rate vs. time for Plumr at 30 °C at 300 rpm mixing speed

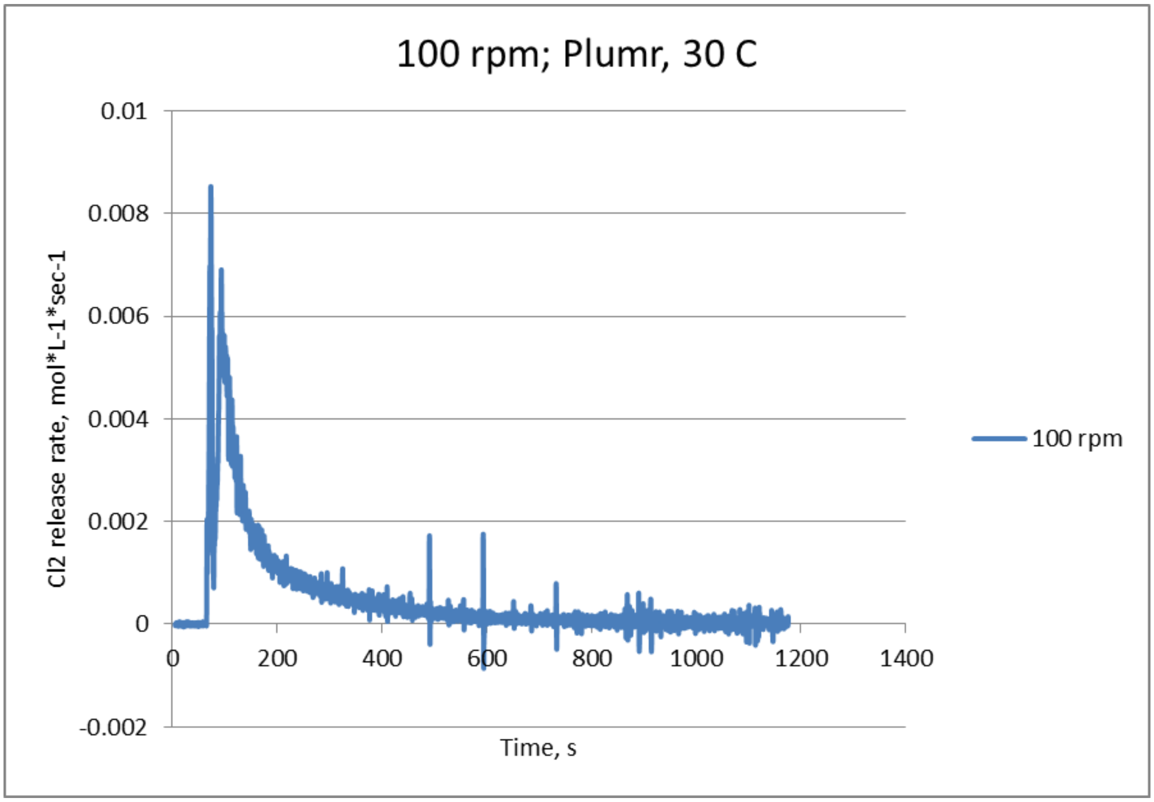


Fig. 128 Instantaneous reaction rate vs. time for Plumr at 30 °C at 100 rpm mixing speed

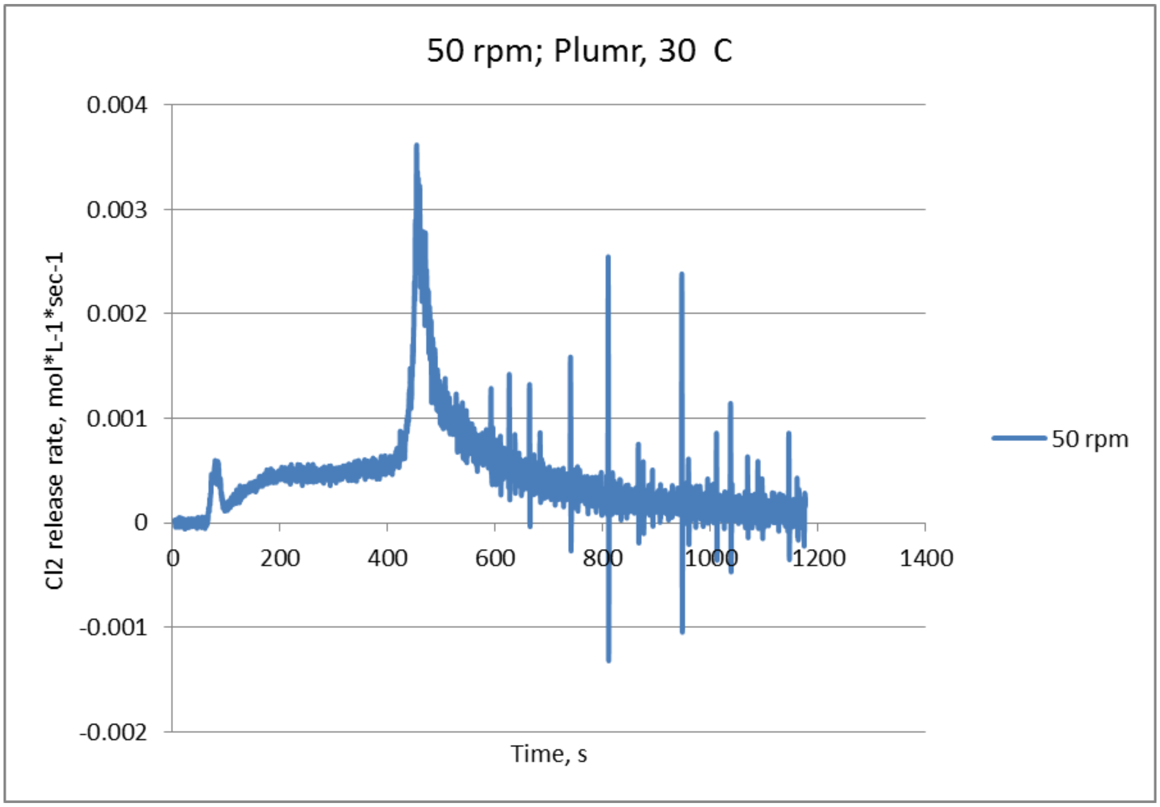


Fig. 129 Instantaneous reaction rate vs. time for Plumr at 30 °C at 50 rpm mixing speed

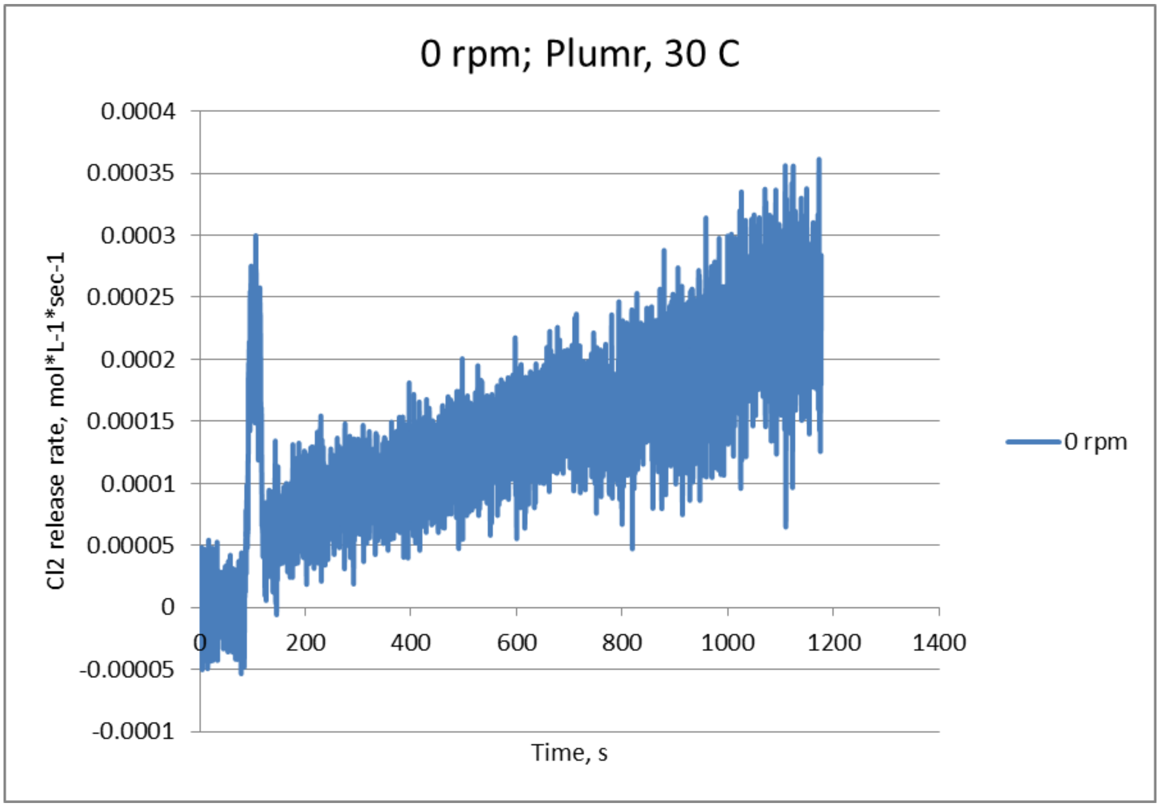


Fig. 130 Instantaneous reaction rate vs. time for Plumr at 30 °C at 0 rpm mixing speed

The plot above shows that the reaction was not completed during the experiment and it accelerated over time. Initially, the reagents did not mix, because acid was added as a laminar flow over the Plumr product and then they diffused one into the other. As a result, the kinetic parameter "t=0" may not exist in this case, because t=0 is the moment where reactants are completely mixed together. In this case, the reaction may end before complete mixing of the reagents occurs. This is quite normal for viscous liquids with no or weak mixing. The highest rate registered in the experiment, in this case, was accepted as the initial rate.

4.4.3.1. Arrhenius Parameters for Liquid Plumr:

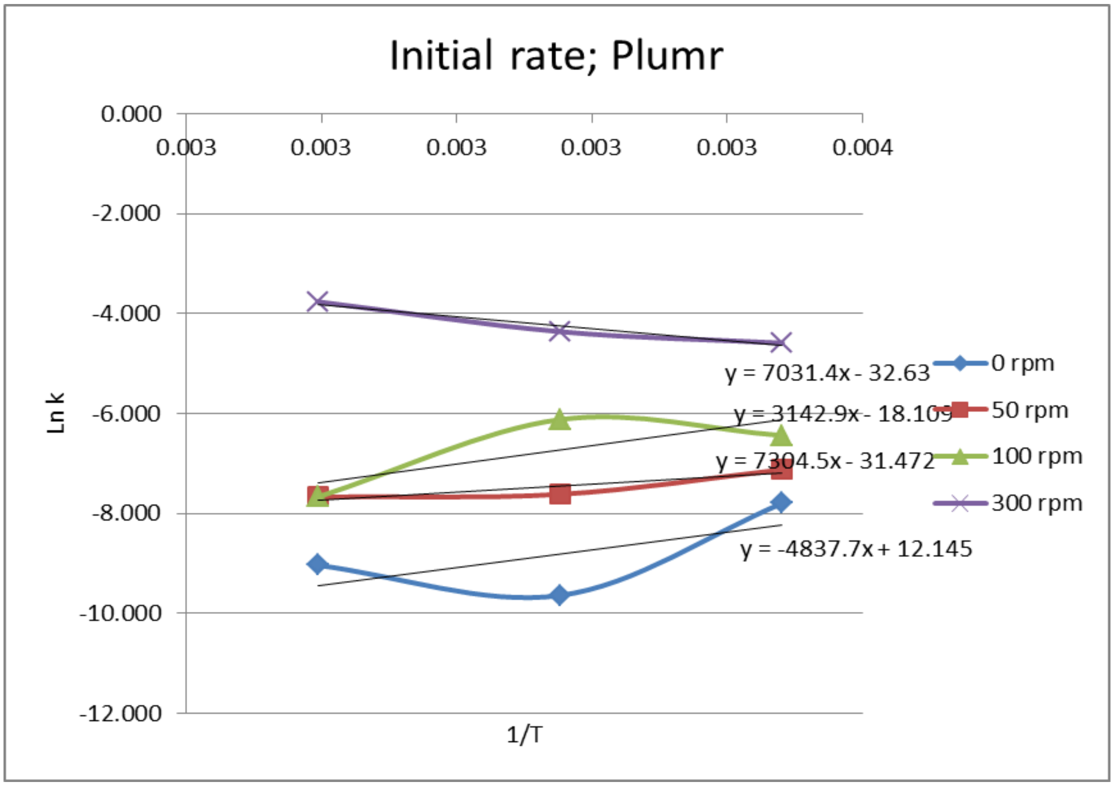


Fig. 131 Arrhenius plots for Plumr – initial rate

Table 37. Initial rate kinetic parameters for Plumr:

Initial	k			
t	0 rpm	50 rpm	100 rpm	300 rpm
15	4.12E-04	8.08E-04	1.60E-03	1.02E-02
22	6.50E-05	4.93E-04	2.20E-03	1.28E-02
30	1.19E-04	4.68E-04	4.68E-04	2.33E-02
1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.003	-7.794	-7.121	-6.438	-4.585
0.003	-9.641	-7.615	-6.119	-4.358
0.003	-9.036	-7.667	-7.667	-3.759
M =	7031.400	3142.900	7304.500	-4837.700
B =	-32.600	-18.109	-31.472	12.145
E_a =	-58.459	-26.130	-60.730	40.221
A=	6.950E-15	1.366E-08	2.147E-14	1.882E+05

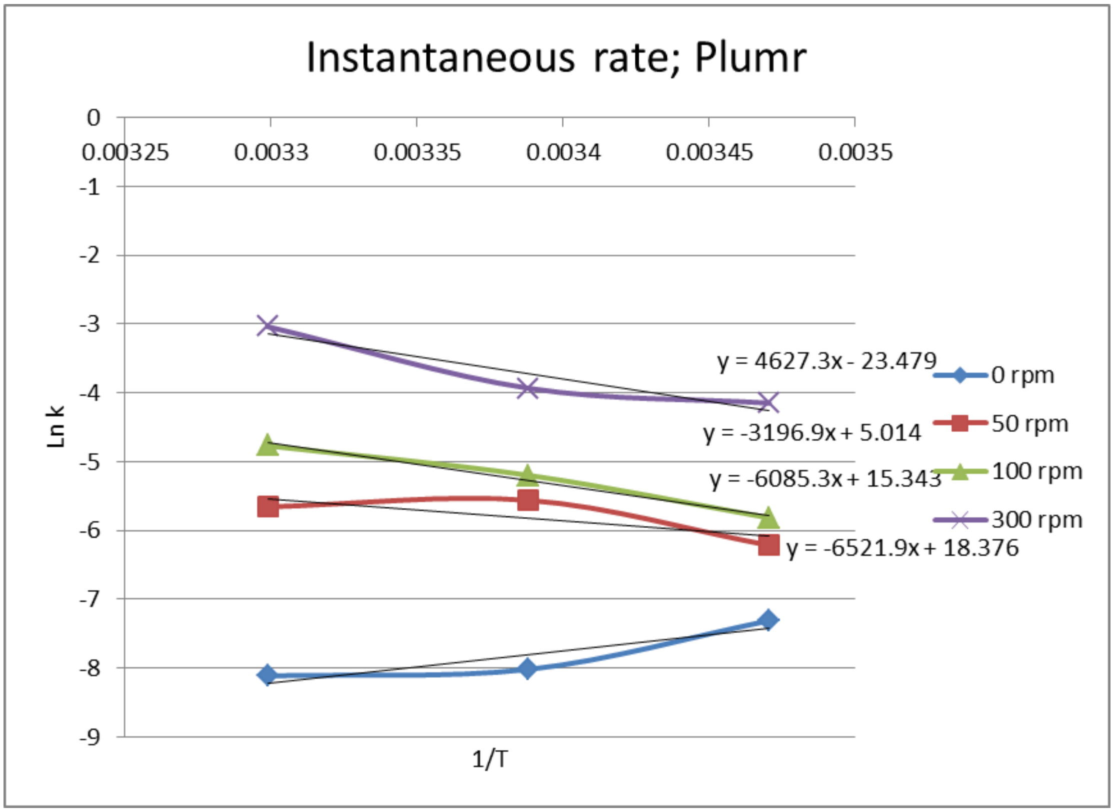


Fig. 132 Arrhenius plots for Plumr – instantaneous maximal point rate

Table 38. Instantaneous rate kinetic parameters for Plumr:

Instant

t, C	0 rpm	50 rpm	100 rpm	300 rpm
15	6.70E-04	2.00E-03	2.98E-03	1.58E-02
22	3.30E-04	3.85E-03	5.53E-03	1.96E-02
30	3.00E-04	3.50E-03	8.50E-03	4.80E-02

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.00347	-7.308	-6.215	-5.816	-4.148
0.00339	-8.016	-5.560	-5.198	-3.932
0.00330	-8.112	-5.655	-4.768	-3.037
M =	4627.3	-3196.9	-6085.3	-6521.9
B =	-23.47	5.01	15.34	18.37
E_a =	-38.471	26.579	50.593	54.223
A=	6.41E-11	1.50E+02	4.59E+06	9.51E+07

In the case of the Liquid Plumr product, the Arrhenius parameters make sense thermodynamically only at the highest mixing speed – 300 rpm. At lower speeds the reaction rate is limited by mixing and diffusion of reactants. (The good indication of this is a negative value of E_a, marked in red in the tables above. Energy of activation may not be negative, however E_a in the Arrhenius equation could account for other temperature-sensitive processes as diffusion, change of viscosity, etc.) As a result chlorine release could take a long time if reactants are not mixed intensely, chlorine release rate could increase over time. The mixture may produce intensive chlorine- filled foam after some time and cause other unexpected adverse effects. Intense mixing of Liquid Plumr with HCl causes chlorine release in a matter of seconds, however with no mixing the release of harmful amounts of chlorine could take more than one hour. In the last case, a sudden increase of chlorine rate is possible at about 30 minutes.

4.4.4. Stabilized chlorinating pucks by hth (Trichloro-S-Triazinetrione) (TCA)

Reactions of Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione) with water were very slow. In the course of the experiment, only a very small fraction of the product reacted with water and accordingly, there was an extremely small change of concentration of it in the water. In addition the reaction mixture had a certain amount of solid product in it that kept the water solution saturated and accordingly at a constant concentration. As a result the reaction rate remained constant during the period of experiment (1 hr). In case of a constant reaction rate, the initial and instantaneous reaction rates are equal, and accordingly we reported only one rate value per experiment.

Trichloro-S-Triazinetrione - 15 °C

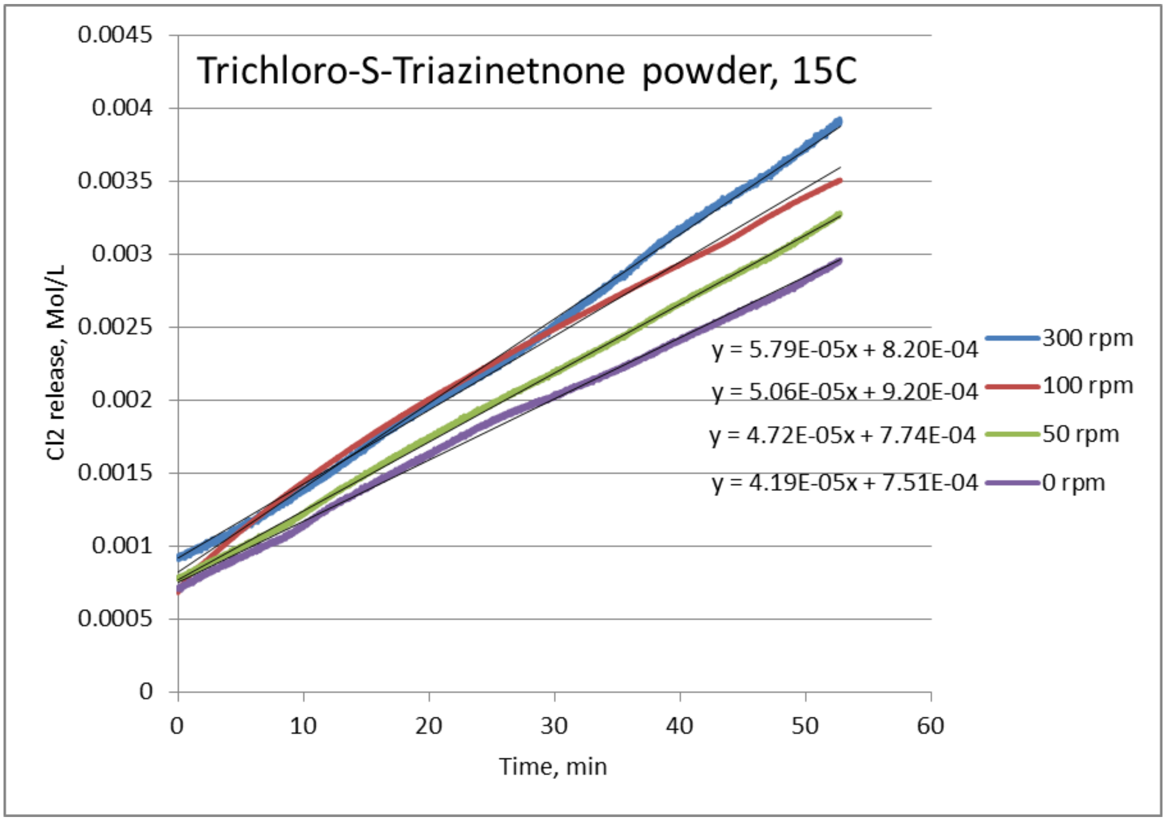


Fig. 133 Chlorine release from Trichloro-S-Triazinetrione reacted with H2O at 15 °C and different mixing speeds

Table 39. Initial rates of chlorine release from Trichloro-S-Triazinetrione at 15 °C:

Speed	Rate
0	6.98E-07
50	7.87E-07
100	8.43E-07
300	9.65E-07

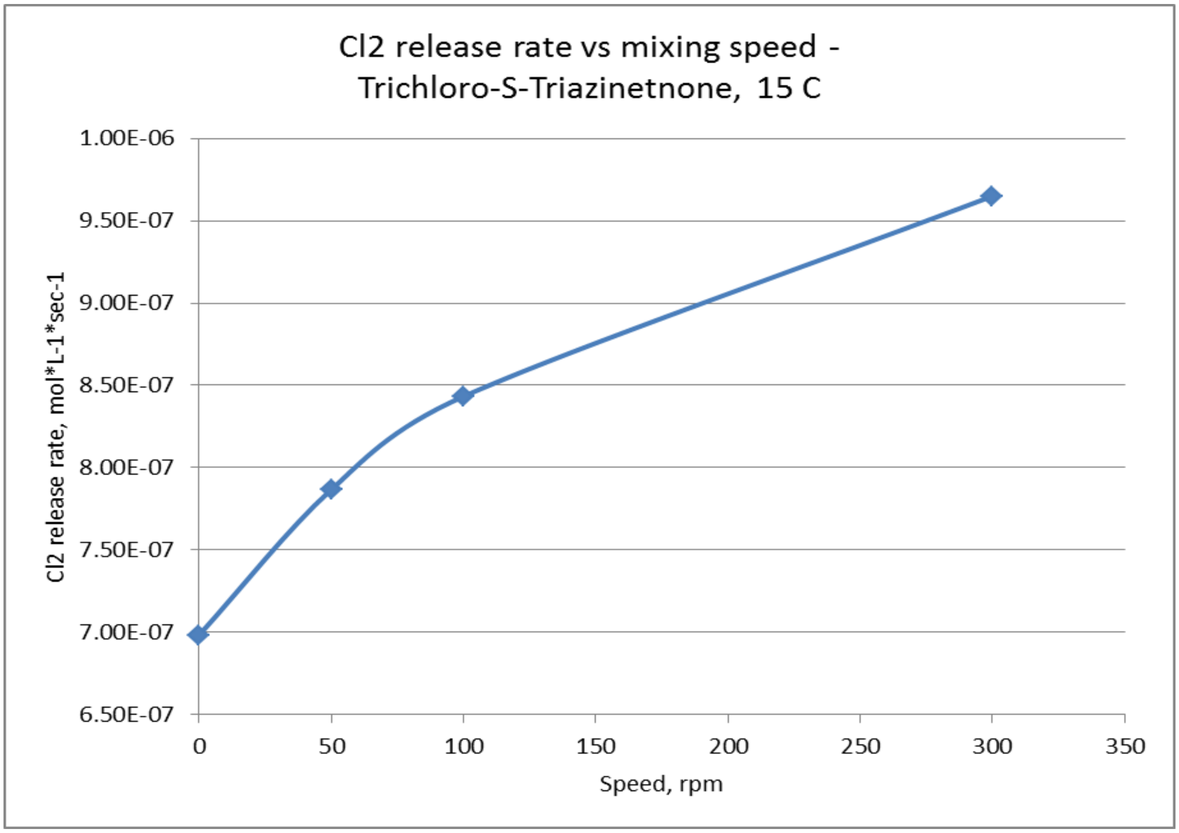


Fig. 134 Chlorine release rate vs. mixing speed for Trichloro-S-Triazinetrione at 15 °C

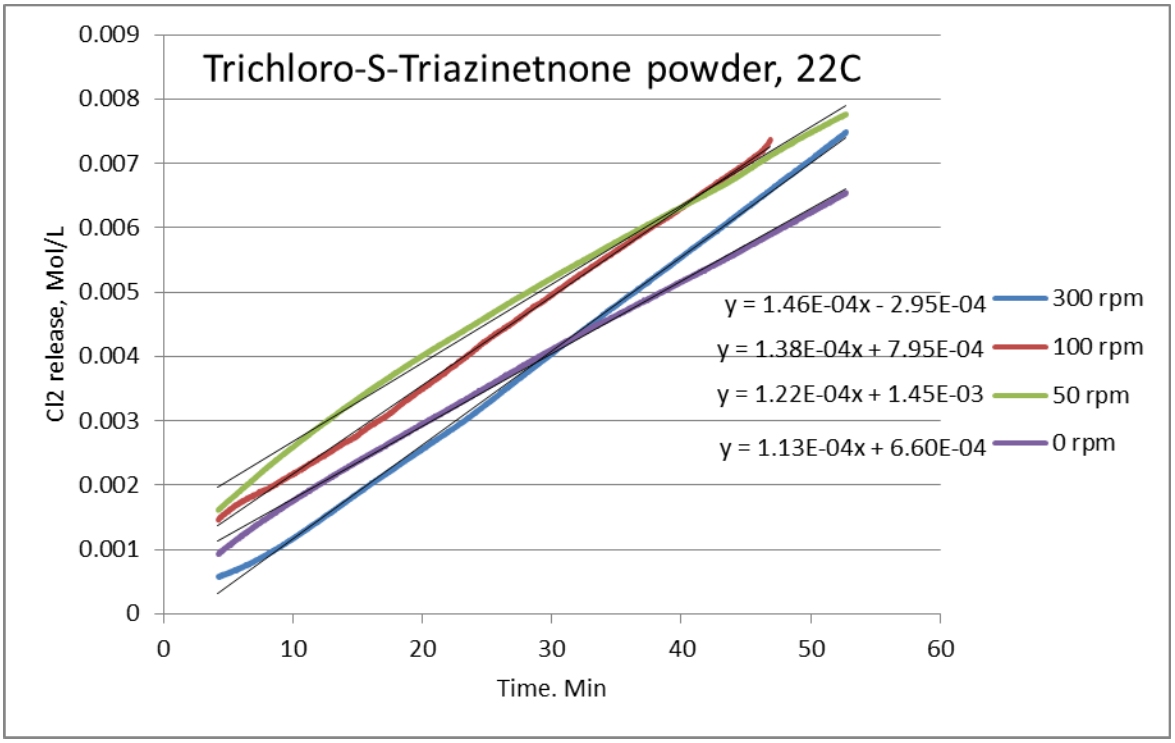


Fig. 135 Chlorine release from Trichloro-S-Triazinetrione product reacted with H2O at 22 °C and different mixing speeds

Table 40. Initial rates of chlorine release from Trichloro-S-Triazinetrione at 22 °C:

Speed	Rate Mol · L^{-1} · s^{-1}
0	1.88E-06
50	2.03E-06
100	2.30E-06
300	2.48E-06

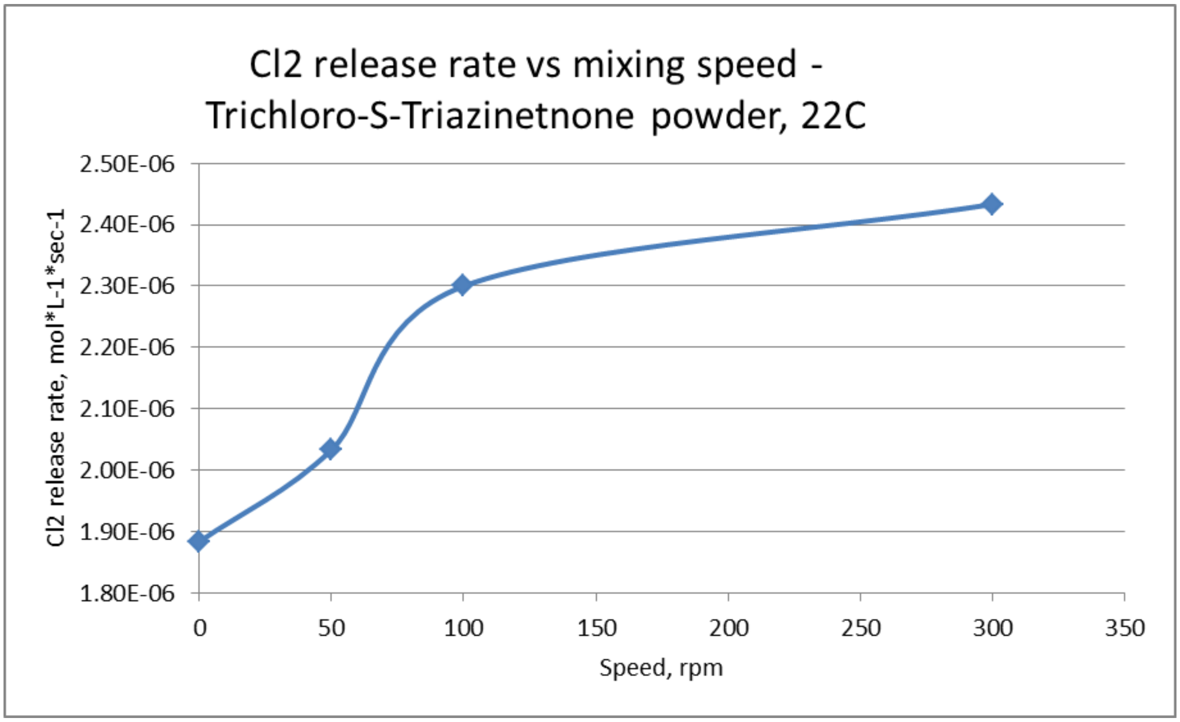


Fig. 136 Chlorine release rate vs. mixing speed for Trichloro-S-Triazinetrione at 22 °C

Trichloro-S-Triazinetrione - 30 °C

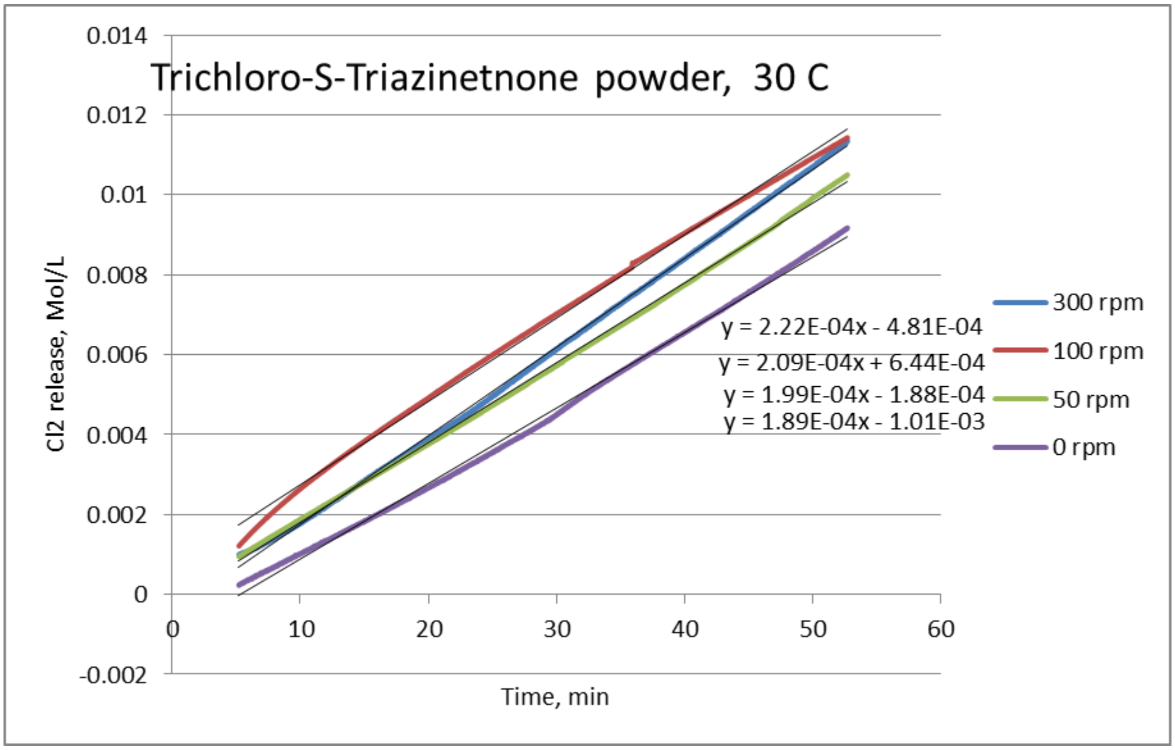


Fig. 137 Chlorine release from Trichloro-S-Triazinetrione product reacted with H2O at 30 °C and different mixing speeds

Table 41. Initial rates of chlorine release from Trichloro-S-Triazinetrione at 30 °C:

Speed	Rate
0	3.15E-06
50	3.32E-06
100	3.48E-06
300	3.72E-06

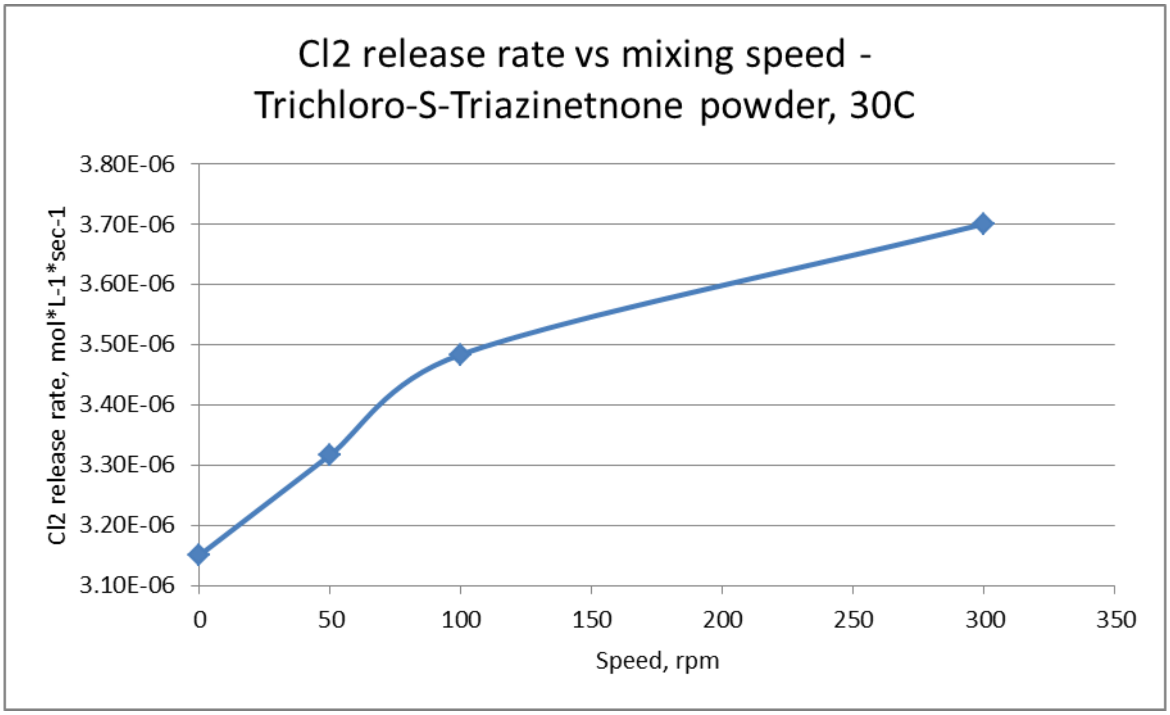


Fig. 138 Chlorine release rate vs. mixing speed for Trichloro-S-Triazinetrione at 30 °C

4.4.4.1. Arrhenius Parameters for Trichloro-S-Triazinetrione:

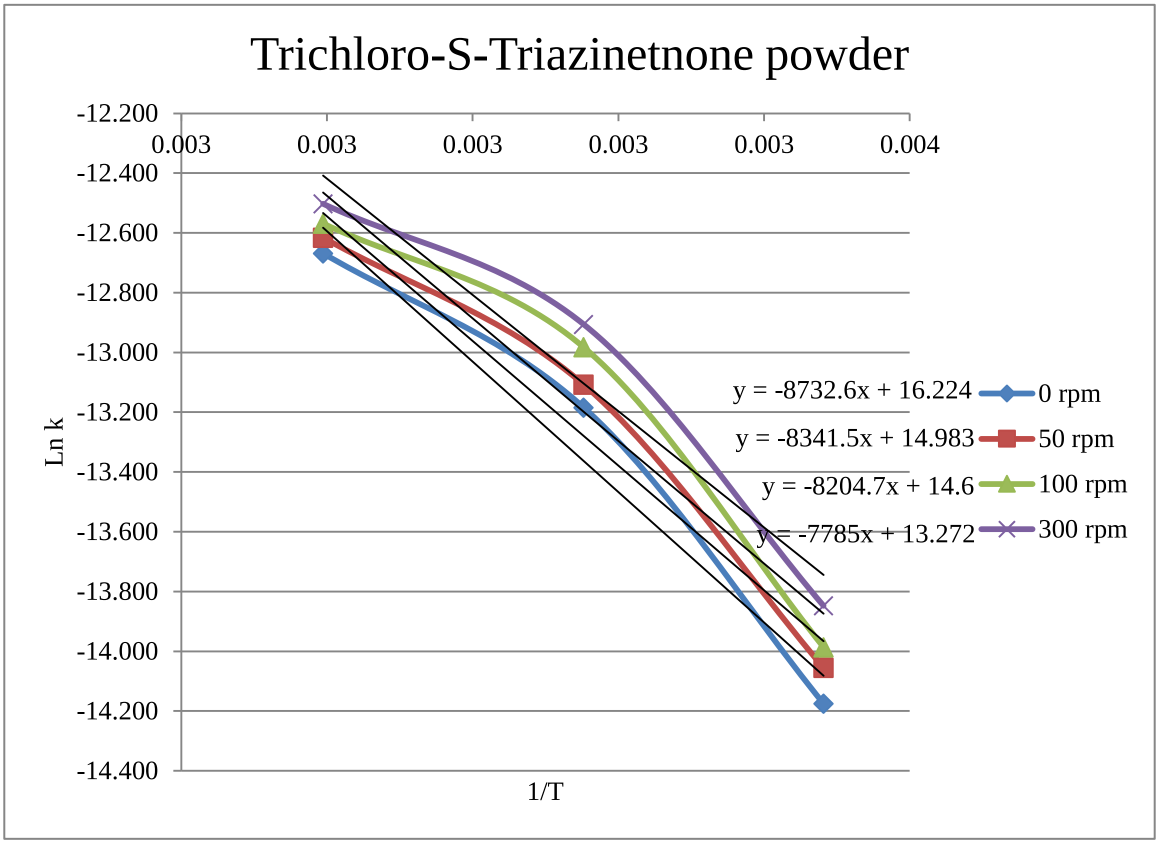


Fig. 139 Arrhenius plots for Trichloro-S-Triazinetrione

Table 42. Kinetic parameters for Trichloro-S-Triazinetrione:

t	0 rpm	50 rpm	100 rpm	300 rpm
15	6.98E-07	7.87E-07	8.43E-07	9.68E-07
22	1.88E-06	2.03E-06	2.30E-06	2.48E-06
30	3.15E-06	3.32E-06	3.48E-06	3.72E-06

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.003	-14.175	-14.055	-13.986	-13.848
0.003	-13.184	-13.107	-12.983	-12.906
0.003	-12.668	-12.616	-12.568	-12.503
M =	-8732.600	-8341.500	-8204.700	-7785.000
B =	16.220	14.983	14.600	13.270
E_a =	72.603	69.351	68.214	64.724
A=	1.107E+07	3.214E+06	2.191E+06	5.795E+05

Certain dependencies of reaction rates and E_a on the mixing speed were detected for Trichloro-S-Triazinetrione. It is uncommon for slow reactions to depend on mixing speed because the time of mixing is very small compared to the time of reaction. For example, if the time required for the reaction to be completed is one year, and mixing of reactants was one or two minutes, then there will be no measurable differences in initial rates.

In the case of Trichloro-S-Triazinetrione, the rate-limiting stage is evaporation of chlorine from the liquid. This shifts the equilibrium of the reaction which could be sensitive to friction, so continuous mixing may promote Cl_2 formation.

4.4.5. Stabilized chlorinating granules by Jacuzzi Sodium (Dichloro-s-triazinetrione dihydrate)

Dichloro-s-triazinetrione dihydrate – 15 °C

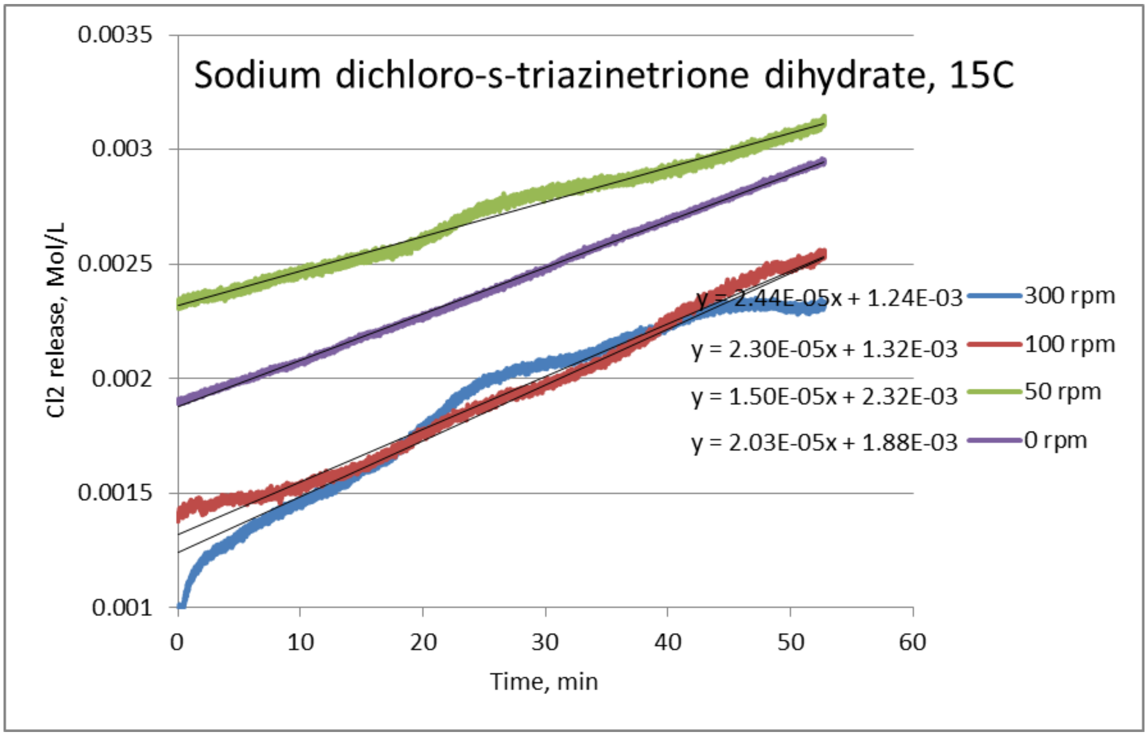


Fig. 140 Chlorine release from Dichloro-s-triazinetrione dihydrate reacted with H2O at 15 °C and different mixing speeds

Table 43. Initial rates of chlorine release from Dichloro-s-triazinetrione dihydrate at 15 °C:

Speed	Rate
0	3.38E-07
50	2.50E-07
100	3.83E-07
300	4.07E-07

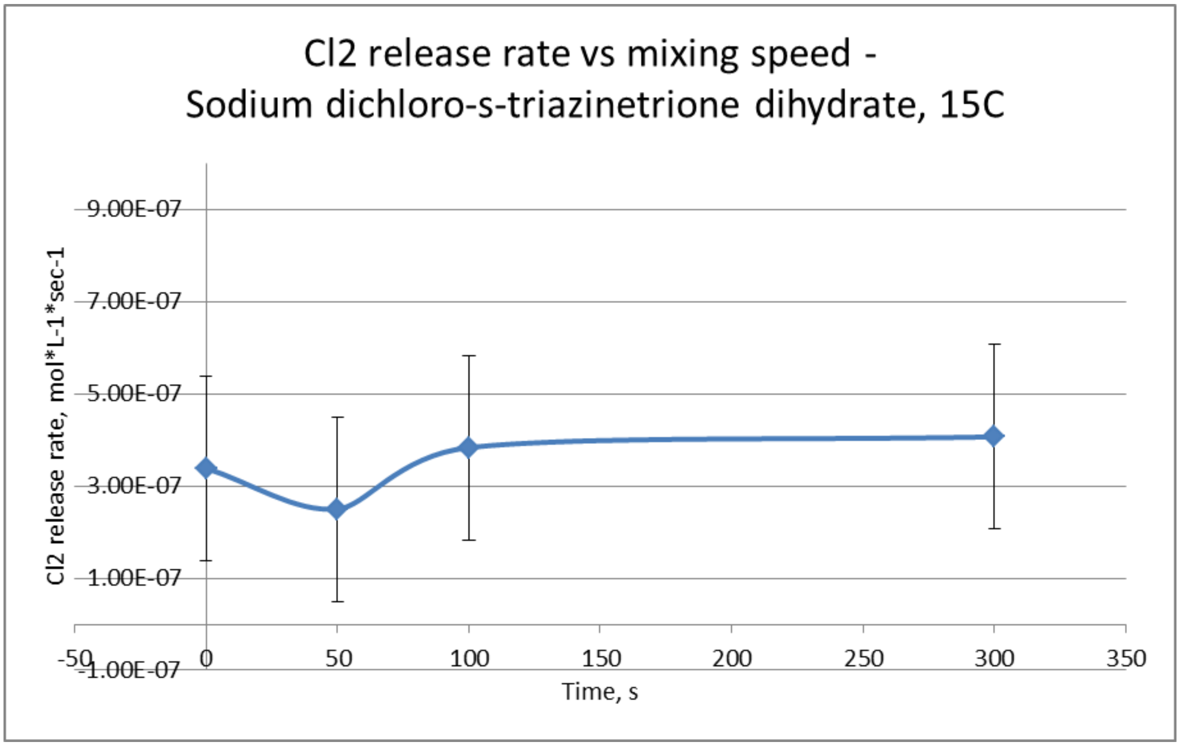


Fig. 141 Chlorine release rate vs. mixing speed for Dichloro-s-triazinetrione at 15 °C.

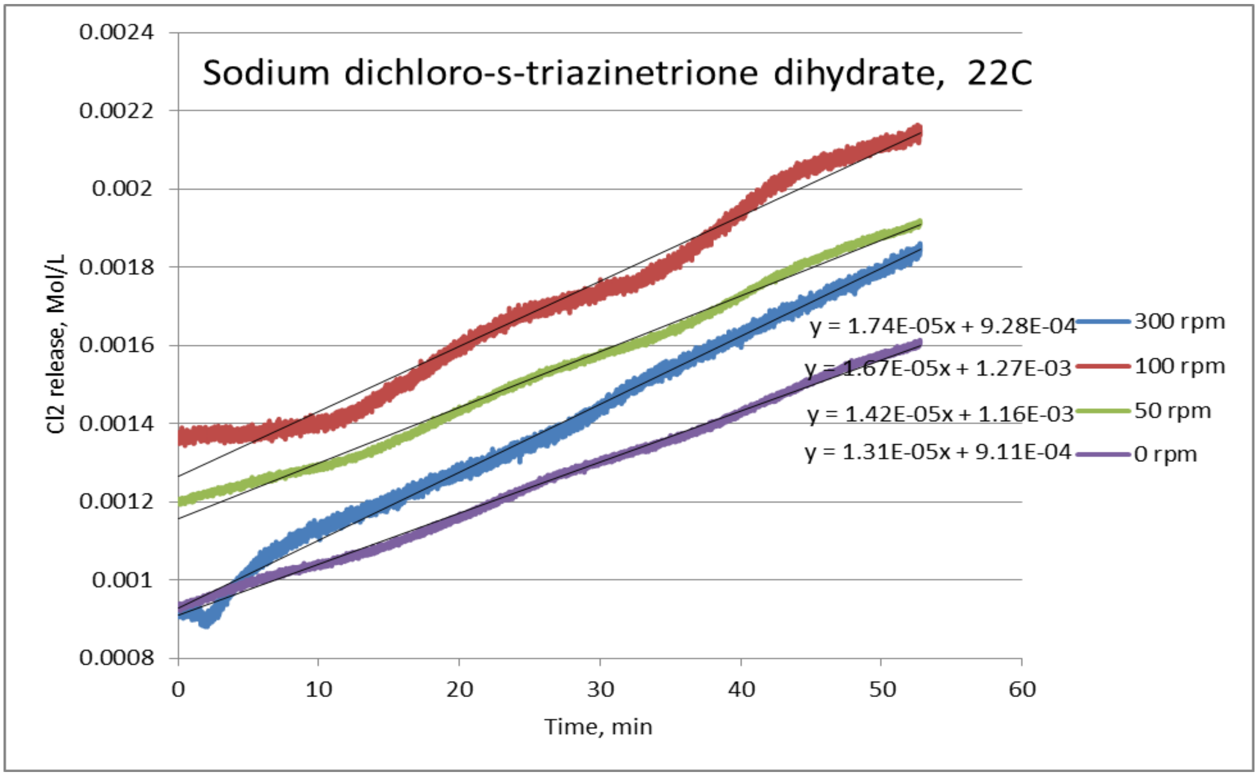


Fig. 142 Chlorine release from Dichloro-s-triazinetrione dihydrate reacted with H2O at 22 °C and different mixing speeds

Table 44. Initial rates of chlorine release from Dichloro-s-triazinetrione dihydrate at 22 °C:

Speed	Rate
0	2.18E-07
50	2.37E-07
100	2.78E-07
300	2.90E-07

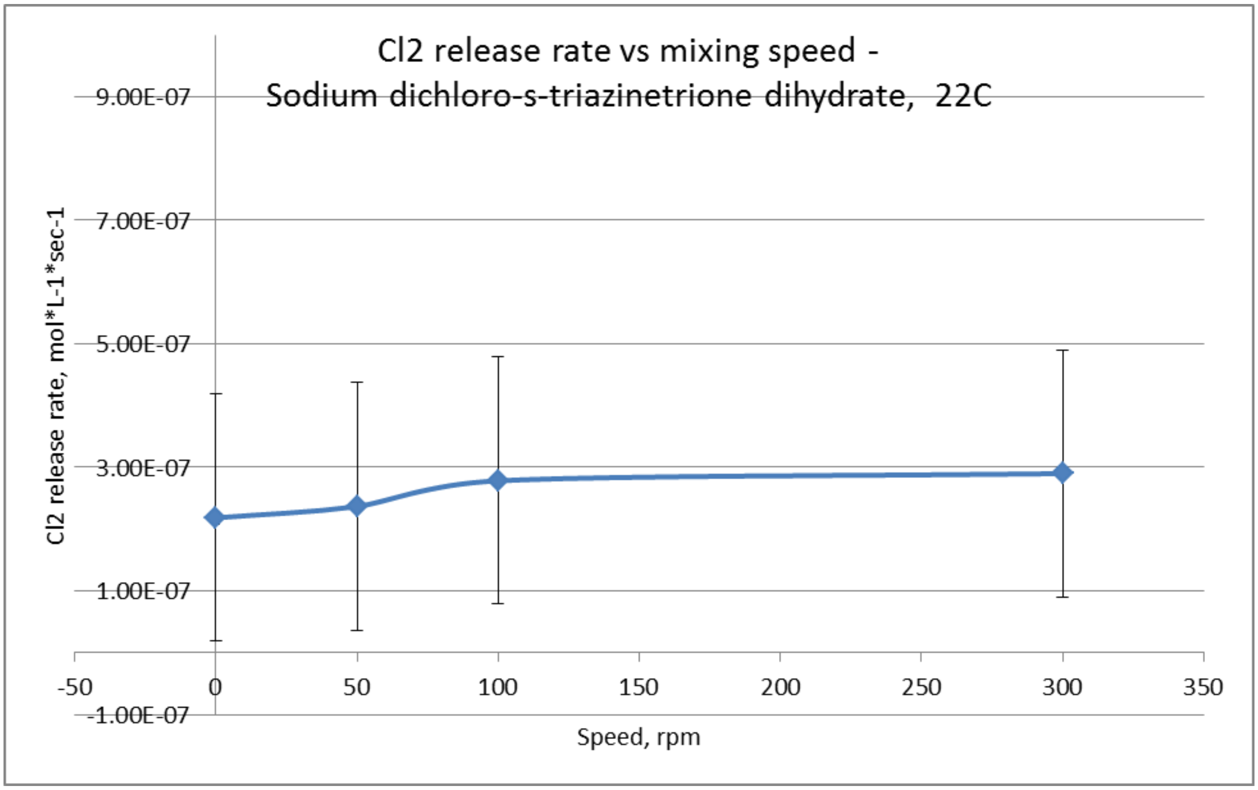


Fig. 143 Chlorine release rate vs. mixing speed for Dichloro-s-triazinetrione at 22 °C

No dependence of reaction rate on the mixing speed was detected.

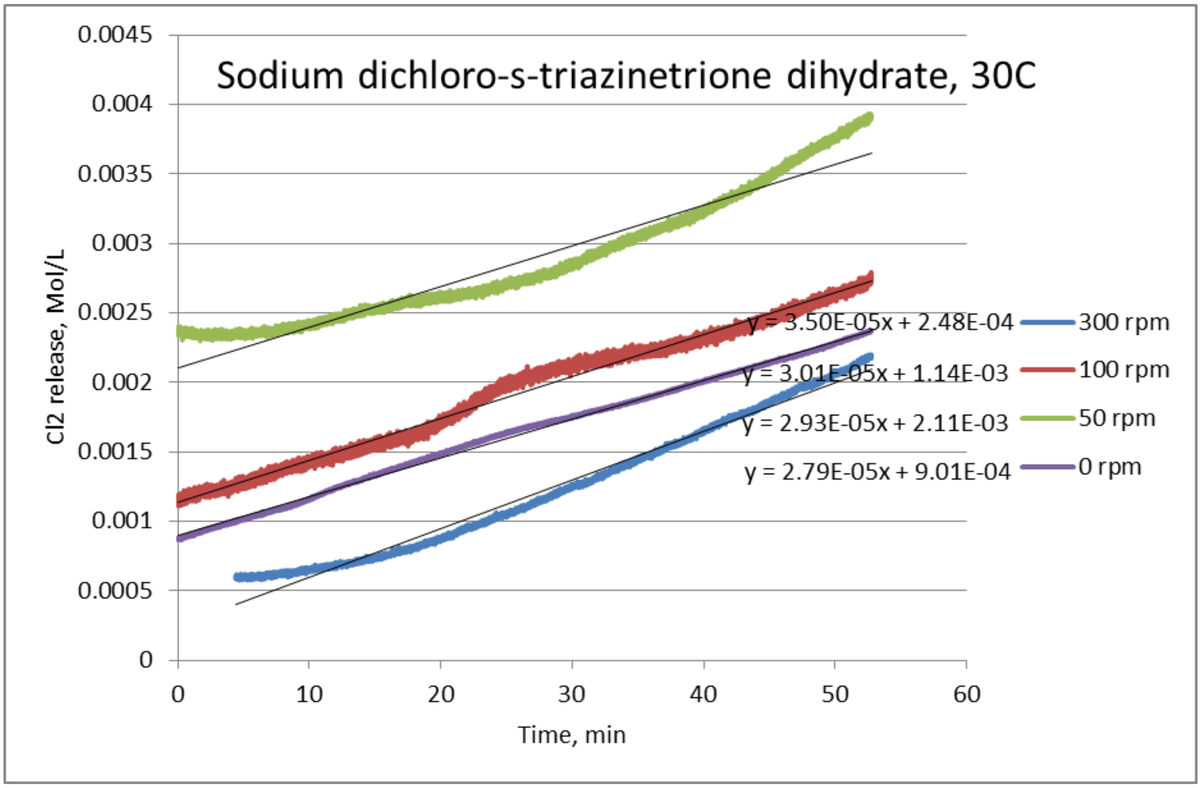


Fig. 144 Chlorine release from Dichloro-s-triazinetrione dihydrate reacted with H2O at 30 °C and different mixing speeds

Table 45. Initial rates of chlorine release from Dichloro-s-triazinetrione dihydrate at 30 °C:

Speed	Rate
0	4.65E-07
50	4.88E-07
100	5.02E-07
300	5.83E-07

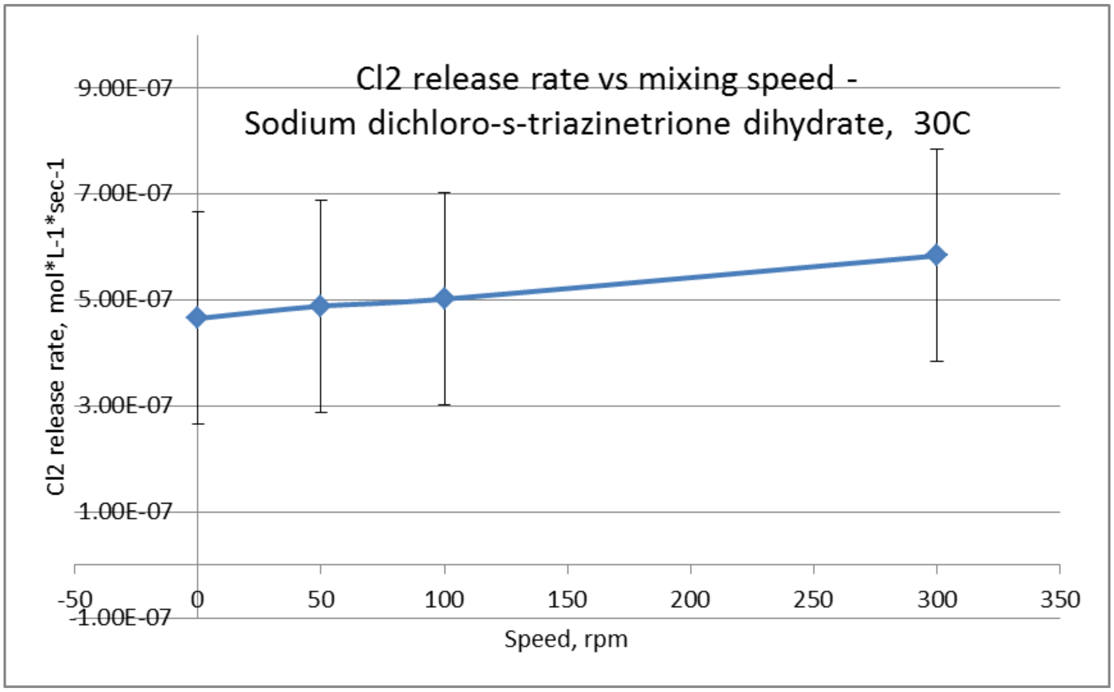


Fig. 145 Chlorine release rate vs. mixing speed for Dichloro-s-triazinetrione at 30 °C

No dependence of reaction rate on the mixing speed was detected.

4.4.5.1. Arrhenius Parameters for Sodium dichloro-s-triazinetrione dihydrate:

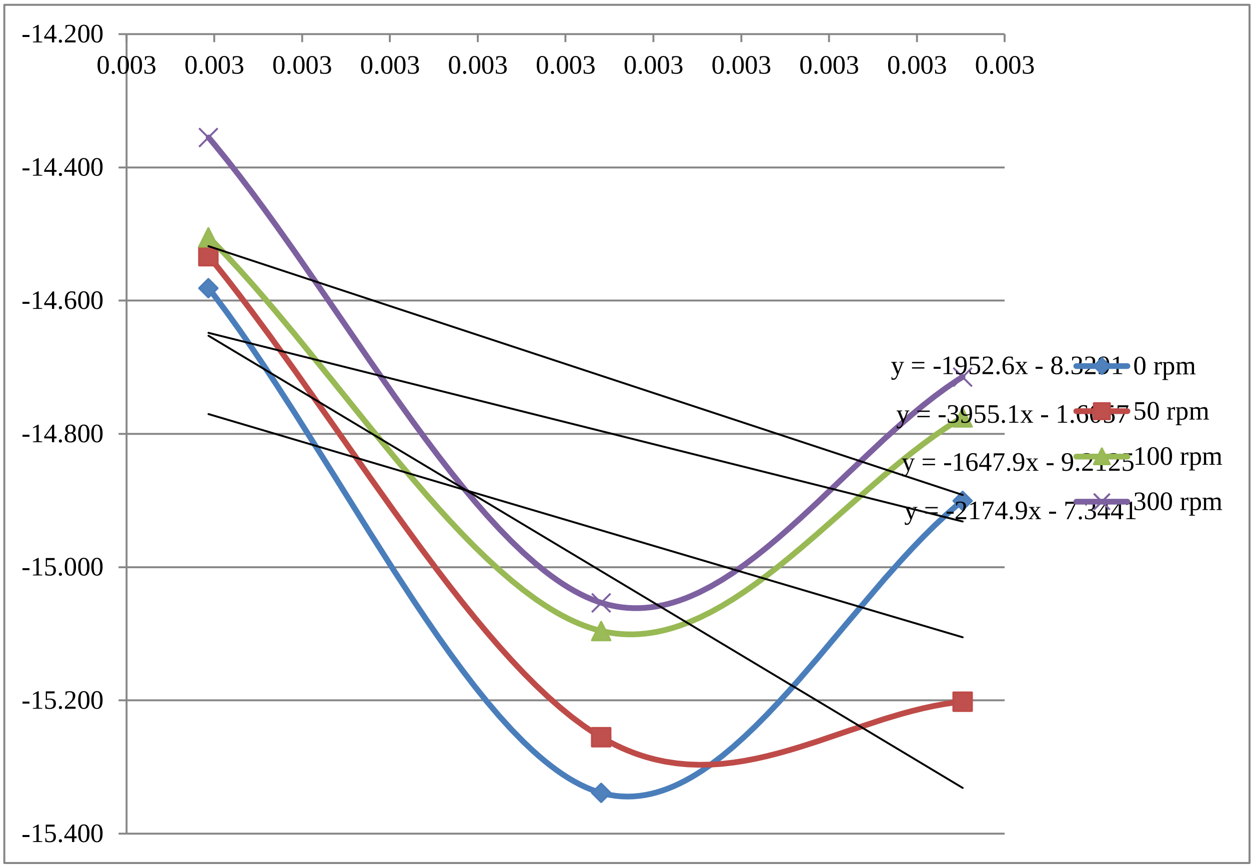


Fig. 146 Arrhenius plots for Sodium dichloro-s-triazinetrione dihydrate

Table 46. Kinetic parameters for Sodium dichloro-s-triazinetrione dihydrate:

t	0 rpm	50 rpm	100 rpm	300 rpm
15	3.38E-07	2.50E-07	3.83E-07	4.07E-07
22	2.18E-07	2.37E-07	2.78E-07	2.90E-07
30	4.65E-07	4.88E-07	5.02E-07	5.83E-07

1/T	0 rpm	50 rpm	100 rpm	300 rpm
0.003	-14.900	-15.202	-14.775	-14.714
0.003	-15.339	-15.255	-15.096	-15.053
0.003	-14.581	-14.533	-14.505	-14.355
M =	-1952.600	-3955.100	-1647.9	-2174.900
B =	-8.320	-1.606	-9.210	-7.344
E_a =	16.234	32.883	13.701	18.082
A=	2.436E-04	2.007E-01	1.000E-04	6.464E-04

Reactions of Stabilized chlorinating granules by Jacuzzi (Sodium dichloro-s-triazinetrione dihydrate) with water were very slow, 3 to 5 times slower than reactions of Stabilized chlorinating puck powder (Trichloro-S-Triazinetrione). Such small reaction rates become comparable with random chlorine concentration fluctuations during the experiments. The detector provided excellent sensitivity, however the water condensate in the reflux condenser from time to time dropped back into the reaction mixture. Because of the difference in temperature in the condenser and the reactor, those droplets released some small but detectable amount of chlorine in the gas phase upon re-heating in the reactor. Accordingly, a “wavy” shape on the chlorine release curve was observed. As a result, this introduced considerable error in the measurement of an already slow reaction rate. In fact, no dependence of mixing speed on reaction rate was observed. The low energy of activation was observed for this product, it is in the range between 16 and 33 kJ/mol. One can expect a fast reaction if E_a is low. However the rate of reaction also depends on the “A” parameter, the pre-exponential factor. In this particular case, “A” is very low; this means that the molecule of Sodium dichloro-s-triazinetrione may react only in a small number of collisions with the reactant caused by a steric configuration of the molecule. So the “successful” collision frequency is small, and even with a small E_a barrier, the reaction rate is low.

4.4.6. Super Shock, by hth (Calcium Hypochlorite)

Super Shock, by hth (Calcium Hypochlorite) while mixed with water produced a lot of heat but only a small release of chlorine was detected, close to the setup sensitivity level. As a result, it was difficult to determine Arrhenius parameters with the acceptable accuracy. As discussed above, calcium hypochlorite powder reacts with liquid water to form a hydrate. Calcium oxide and calcium chloride are always present in such products as impurities and they also can react with water and release heat. The chlorine gas however is not released in this process.

The results of measurement of the chlorine release from calcium hypochlorite product at different temperatures and mixing speeds are presented on the pictures below.

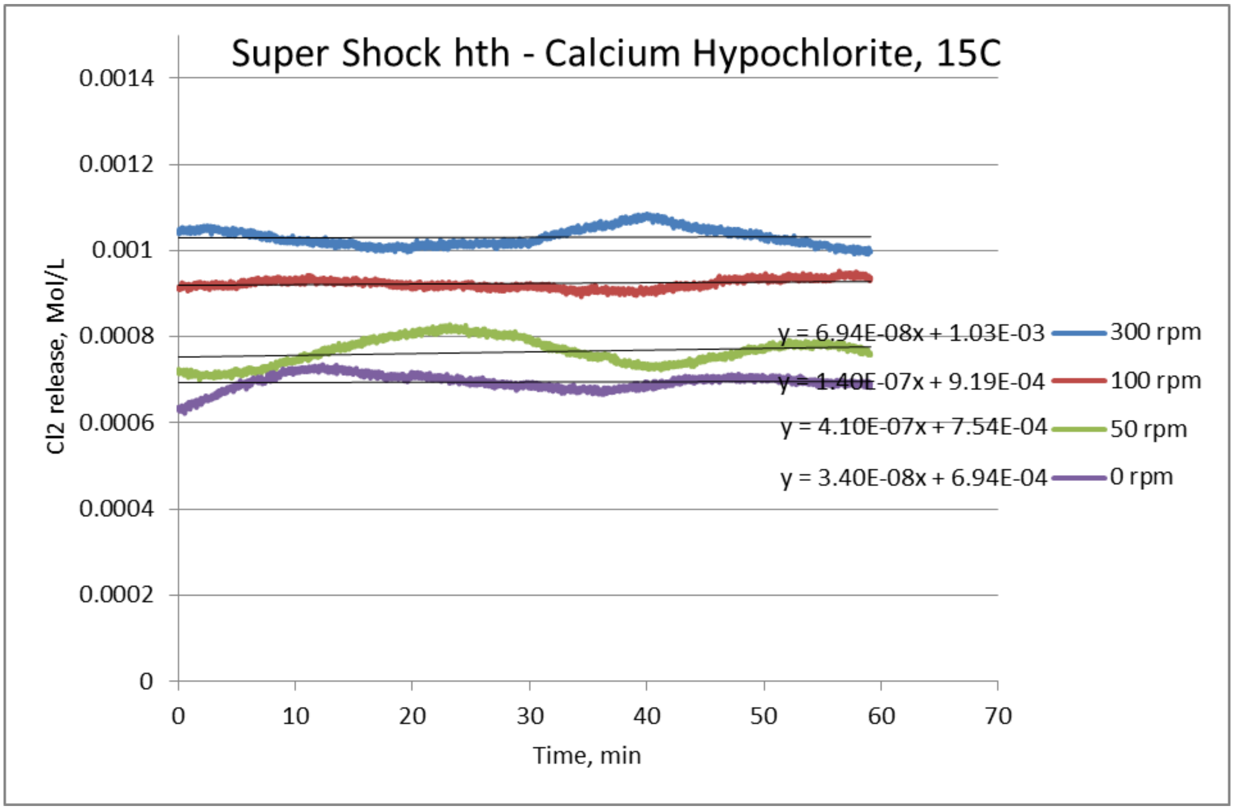


Fig. 147 Chlorine release from Calcium Hypochlorite reacted with H2O at 15 °C and different mixing speeds

Table 47. Initial rates of chlorine release from Calcium Hypochlorite at 15 °C:

Speed	Rate
0	5.67E-09
50	6.83E-09
100	2.33E-09
300	1.16E-09

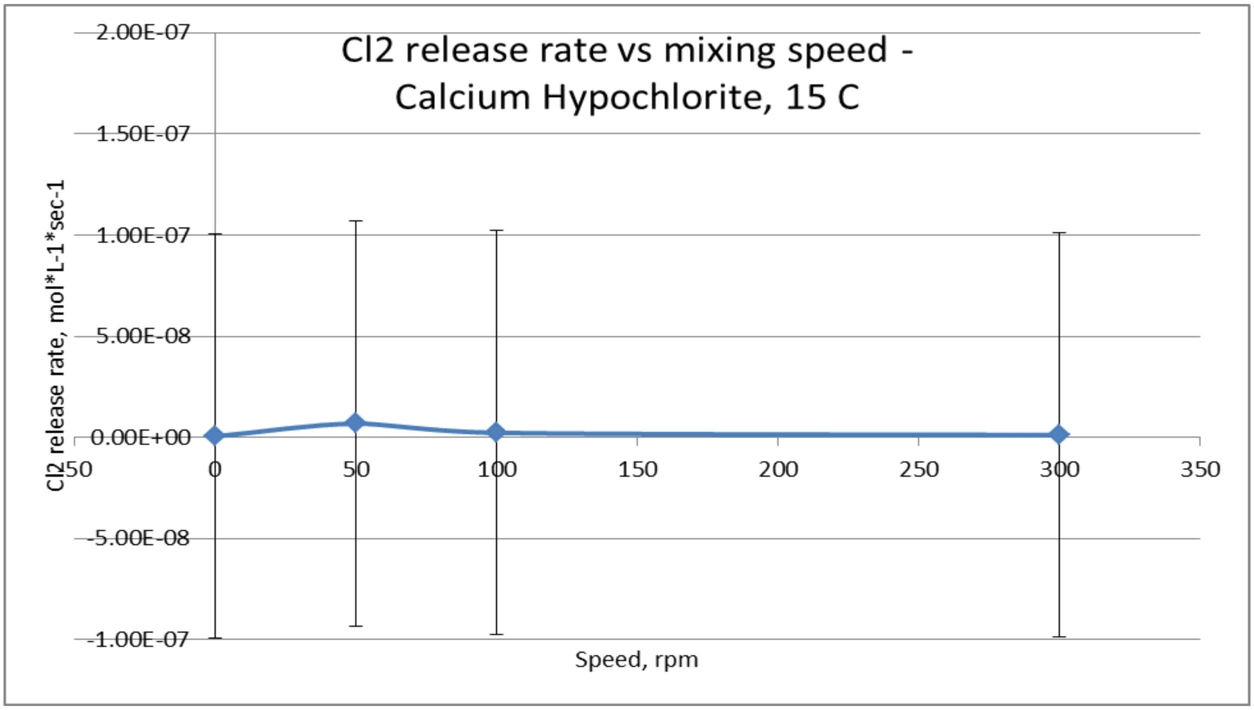


Fig. 148 Chlorine release rate vs. mixing speed for Calcium Hypochlorite at 15 °C

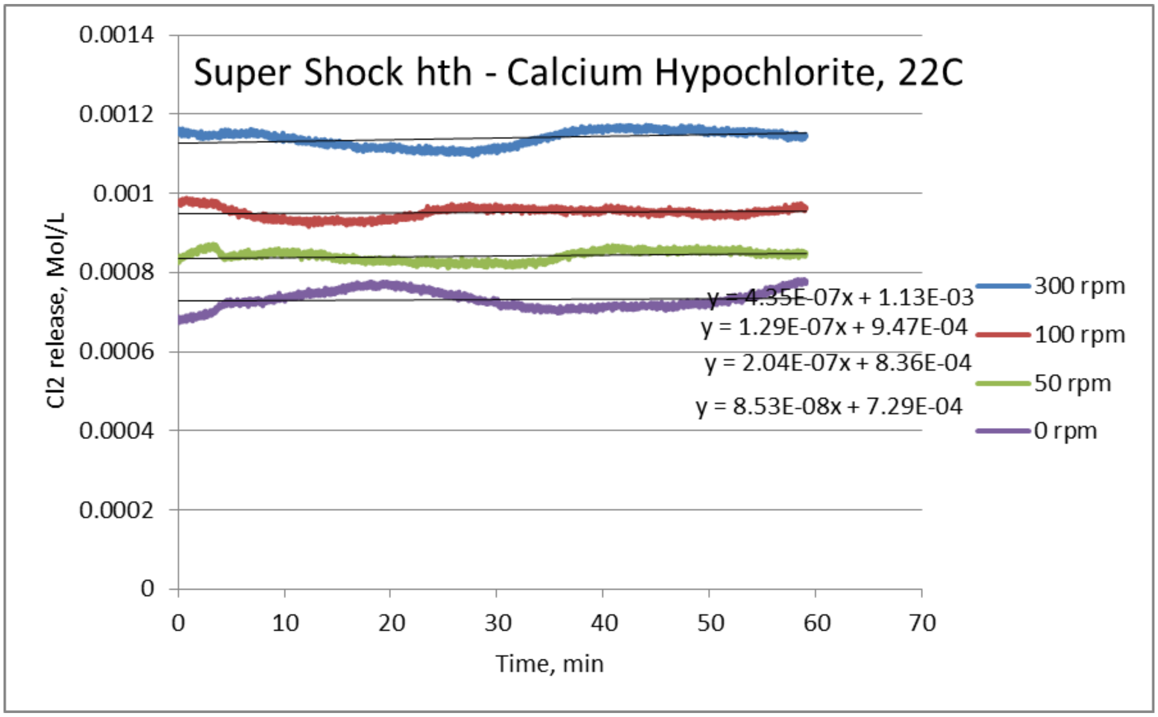


Fig. 149 Chlorine release from Calcium Hypochlorite reacted with H2O at 22 °C and different mixing speeds

Table 48. Initial rates of chlorine release from Calcium Hypochlorite at 22 °C:

Speed	Rate
0	1.42E-09
50	3.40E-09
100	2.15E-09
300	7.25E-09

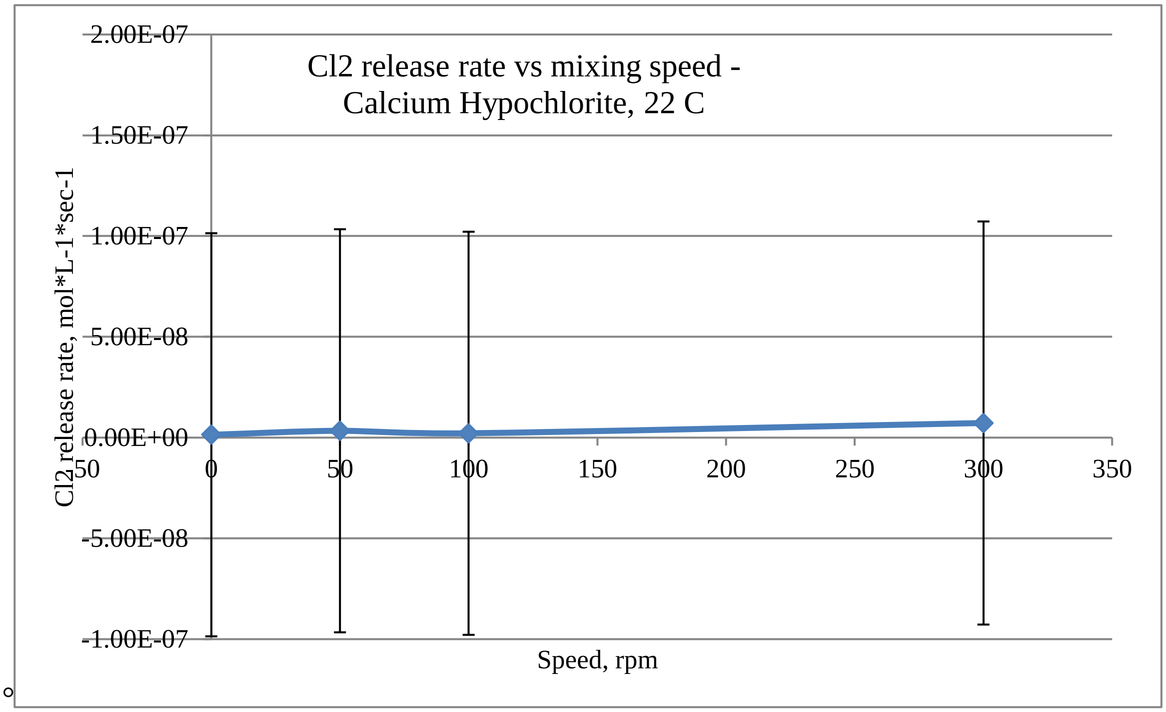


Fig. 150 Chlorine release rate vs. mixing speed for Calcium Hypochlorite at 22 °C

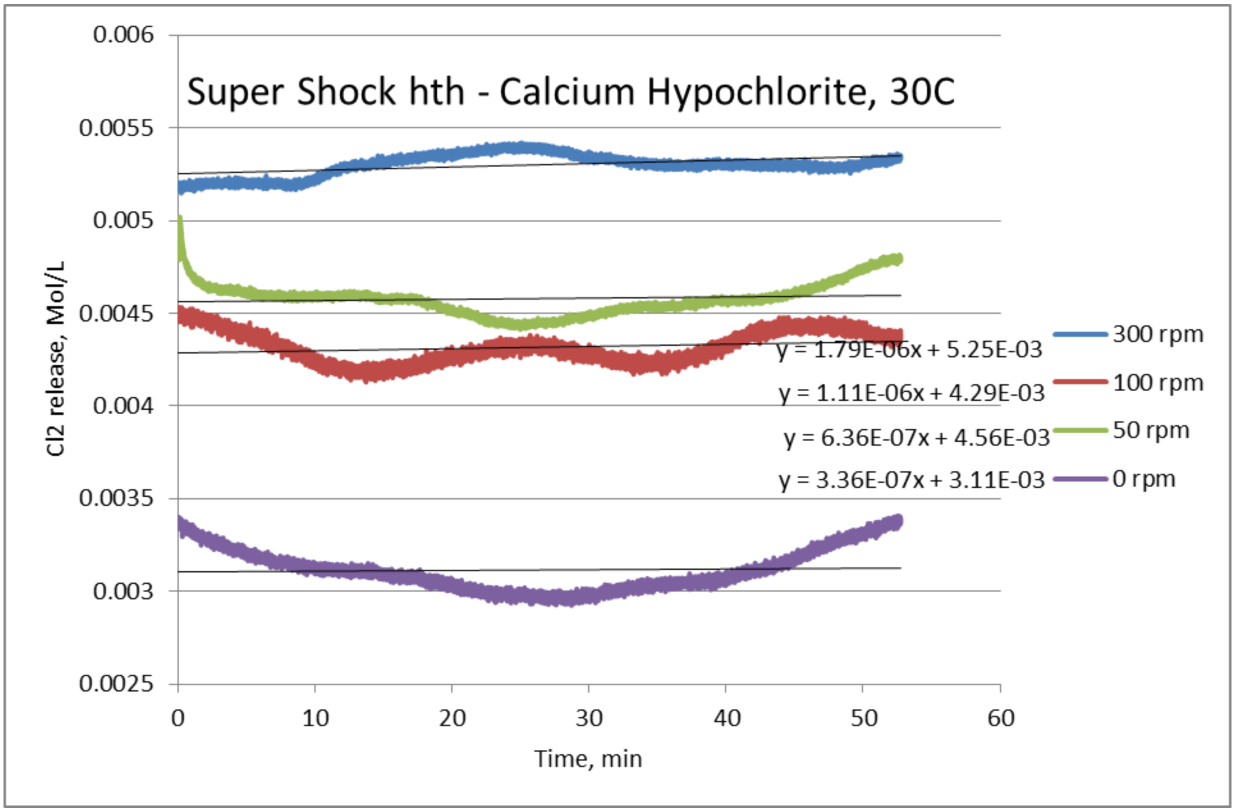


Fig. 151 Chlorine release from Calcium Hypochlorite reacted with H2O at 30 °C and different mixing speeds

Table 49. Initial rates of chlorine release from Calcium Hypochlorite at 30 °C:

Speed	Rate
0	5.60E-10
50	1.06E-08
100	1.85E-08
300	2.98E-08

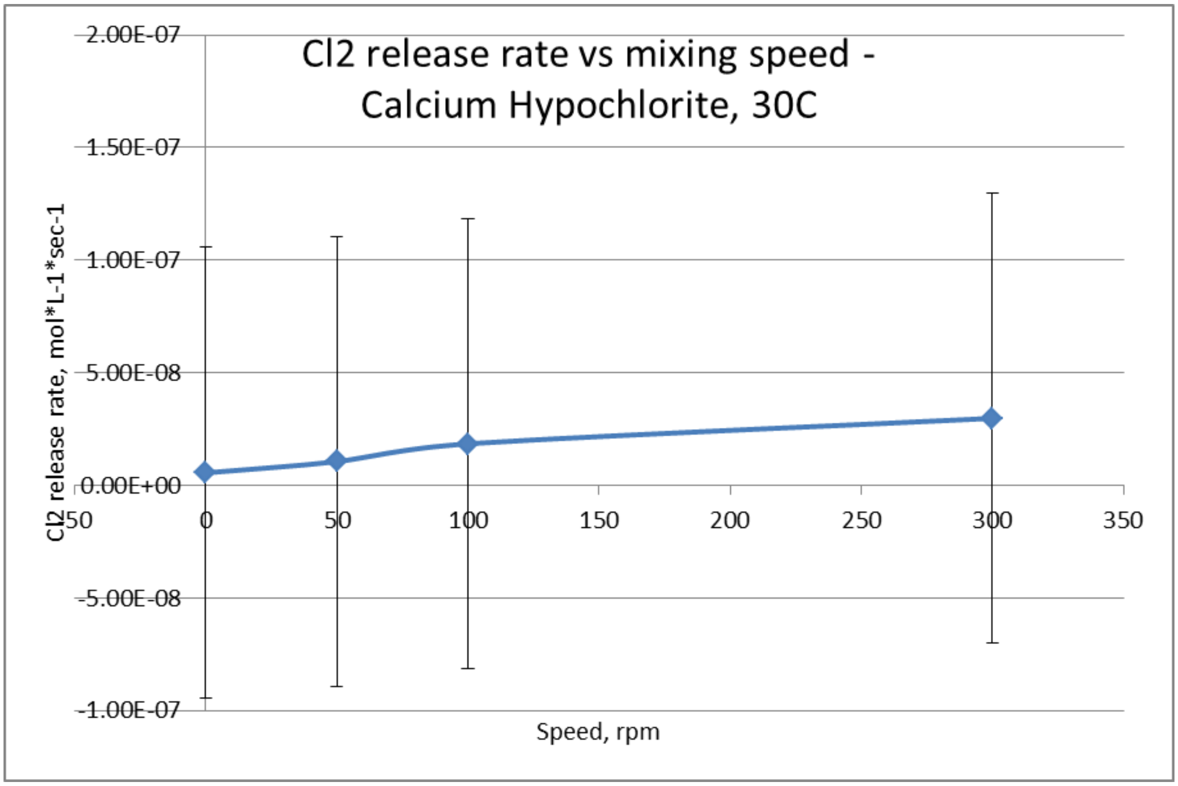


Fig. 152 Chlorine release rate vs. mixing speed for Calcium Hypochlorite at 30 °C

Generally for the calcium hypochlorite product was not found measurable dependence of reaction rate on the mixing speed.

4.4.7. Conclusion for Task 4:

In Task 4 experiments, reaction rates of 3 liquid and 3 solid products were measured and the dependencies of chlorine gas release rates on the temperature and the mixing speed were determined. For all products; the chlorine release rate increases with increase of the reaction temperature. However for the liquid hypochlorite products, the mixing speed was the main rate determining parameter. Chlorine gas release rate from liquid products could be increased in two orders of magnitude just because of intensive mixing. (Ex - comparing chlorine release rates from Liquid Plumr at 0 rpm and 300 rpm). This information proves that a product user is at high risk because of a very high chlorine release rate upon mixing.

In general, solid hypochlorite products did not cause a significant chlorine gas release when mixed with water regardless of the initial temperature and the mixing speed. Hence, intensive mixing of solid products with water should not cause substantial danger to a product user.

5. Conclusion

In the project T8080-170164 a number of experiments were conducted with liquid and solid products containing sodium hypochlorite, calcium hypochlorite, Trichloro-S- Triazinetrione and Sodium dichloro-s-triazinetrione dihydrate.

The dependency of quantity of released chlorine gas from sodium hypochlorite solutions at different concentration based on the quantity of added hydrochloric acid was determined. The neutralization (calibration) curves, their temperature dependencies and the pH (~7) at which chlorine release initiates were also obtained. Additionally, the amount of HCl required for initiation of chlorine release linearly depends on the sodium hypochlorite concentration.

The dependency of a quantity of released chlorine gas from calcium hypochlorite on the quantity of added water at different temperatures was studied. It was found that the release of chlorine does not depend on the amount of water added to calcium hypochlorite. The thermal effects of hypochlorite reactions with HCl or water were also recorded.

Chlorine release efficiencies for 3 liquid and 3 solid hypochlorite products were measured in reactions of liquid products with hydrochloric acid, chlorine release efficiencies were in the range of 80.5 to 99.1 % off the theoretically expected values depending on the product and temperature. Increasing the temperature generally increased the chlorine release efficiencies of the liquid product in reactions with HCl. Chlorine release efficiencies from reactions of solid products with water were difficult to determine because of very slow reaction rates; instead, release of chlorine during a one-hour period was reported.

A kinetic study of reactions of 3 liquid products with HCl and 3 solid products with water was performed. Chlorine release rates from liquid products appeared to be very high: Ultra San and Javel-12 had similar rates of chlorine release, regardless of the 2% NaClO concentration difference. The reactions started instantly and the majority of the chlorine release happened within a few seconds after the acid addition. The chlorine release rate at 30 °C did reach $0.5\ \mathrm{mol \cdot L^{-1} \cdot s^{-1}}$, this means that from one liter of product, 12 liters of chlorine would be released during the first second of the reaction. This could form a large, extremely toxic chlorine gas cloud which could cause a potentially fatal poisoning. The third liquid product, Liquid Plumr, had approximately 10 times slower chlorine release rate ($0.05\ \mathrm{mol \cdot L^{-1} \cdot s^{-1}}$as maximum). 1 liter of Liquid Plumr released about 1.2 L of chlorine during the first second and this is still dangerous in the event of an accident. Energies of activation E_a for Ultra San and Javel-12 appeared to be quite similar and equal approximately 25 kJ/Mol. Energy of activation for Liquid Plumr was more than two times higher than for other liquid products (74 kJ/Mol). This is because of complicated composition of this product; it has additives that can cause a high viscosity that decreases by 10 times the rate of the reaction. Viscosity of Liquid Plumr could decrease with increased temperature. As a result, the reaction rate becomes more dependent on the temperature.

The solid products studied released chlorine at a very small rate: 2.48E-06 mol·L^{-1}·s^{-1} (22 °C) for Trichloro-S-Triazinetrione; 2.90E-07 mol·L^{-1}·s^{-1} (22 °C) for Sodium dichloro-s-triazinetrione dihydrate; almost zero for calcium hypochlorite. Wetting of tested solid products may pose no immediate danger, however in a closed, not ventilated room or a closed vessel Trichloro-S-Triazinetrione and Sodium dichloro-s-triazinetrione dihydrate combined with water can create a potentially dangerous chlorine concentration. One kilogram of wet Trichloro-S-Triazinetrione can release 21 mL of chlorine by hour and wet Sodium dichloro-s-triazinetrione dihydrate can release 2.5 mL of chlorine by kg by hour. Calcium hypochlorite appeared to be the least reactive, and no chlorine release was detected, however, it is a highly toxic and active compound that contains a lot of active chlorine and it can violently react with compounds and products other than water, so it may not be considered as 100% “safe”.

The influence of mixing speed on the rate of chlorine release was assessed. The kinetic parameters of reactions of 3 liquid products with 10% HCl and 3 solid products with water at 3 temperatures (15, 22, and 30°C) and at 4 different mixing speeds (0, 50, 100 and 300 rpm) were calculated. It was found that the reaction rates of chlorine release from the liquid products strongly depended on mixing speed. At low mixing speed, mixing and diffusion become rate-determining steps of the reaction and it is not controlled by thermodynamics as it was at a high speed. At low mixing speeds (0 to 50 rpm) the Arrhenius parameters lose their thermodynamic meaning; E_a often becomes negative; however, they may be used as empirical values that describe overall system response to the temperature change. Liquid Plumr exhibited the most dramatic dependence of mixing speed on chlorine release rate. This was caused by the very high viscosity of Liquid Plumr. At the speed zero, only 1/3 of it becomes mixed with the acid to during the entire time of the experiment. In case of Liquid Plumr product, the Arrhenius parameters have thermodynamic sense only at the highest mixing speed – 300 rpm. At lower speeds, the reaction rate is limited by mixing and diffusion of reactants. As a result, chlorine release could take a long time if reactants are not mixed intensively, chlorine release rate could increase over some time. Additionally, the mixture may produce intensive chlorine- filled foam after some time and cause other effects that could not be expected by a product user. Certain dependencies of reaction rates and E_a on the mixing speed were detected for Trichloro-S-Triazinetrione. It is uncommon for slow reactions to depend on mixing speed. Other solid products tested within the project while combined with water did not increase the chlorine release rate with increased mixing speed. As a result, intensive mixing of the solid products with water may not cause by itself a substantial danger to a product user.

6. Summary of Key Findings

6.1. Liquid hypochlorite products

Liquid bleaching products based on sodium hypochlorite release large quantities of dangerous chlorine gas when acidified such as mixing with acid containing solutions. The amount of chlorine gas released is dependent on the active chlorine concentration in the product, temperature, pH of the solution, and speed of mixing.

In Table 50, results are reported for the titration of the commercial hypochlorite products studied in the project. 50 mL of each product was titrated with 10% HCl at 3 temperatures (15, 22 and 30 °C). The 10% hydrochloric acid was introduced as a continuous flow into the reactor at a constant flow rate of 20 $mL \cdot L^{-1} \cdot min^{-1}$ (the flow rate expressed as mL of acid per 1 liter of product per minute). In Table 48 (from left to right) quantity of acid, required for neutralization of a product (to reach pH=7); time to reach neutralization (pH=7); quantity of acid required to add into a product to initiate chlorine release; time when chlorine was first detected; amount of acid, required to reach pH=0.5 at which sodium hypochlorite was completely converted to chlorine gas; and time to reach pH=0.5 were reported.

Units of hydrochloric acid quantity: mL/L – milliliters of 10% HCl per 1 liter of a product.

Table 50. Titration results of commercial liquid products based on NaClO at 20 $mL \cdot L^{-1} \cdot min^{-1}$ of 10% hydrochloric acid flow rate.

Temp., °C	Product	[HCl] to pH=7, mL/L	time to pH=7, min	[HCl] to Cl_2 first detection, mL/L	Time to Cl_2 first detection, min	[HCl] to pH=0.5, mL/L	time to pH=0.5, min
15	Ultra San, ECOLAB	240	12	248	12.4	680	34
22	Ultra San, ECOLAB	210	10.5	200	10	520	26
30	Ultra San, ECOLAB	180	9	160	8	400	20
15	Javel 12, by SANY	200	10	200	10	700	35
22	Javel 12, by SANY	190	9.5	200	10	640	32
30	Javel 12, by SANY	180	9	200	10	600	30
15	Liquid Plumr, Clorox	250	12.5	330	16.5	570	28.5
22	Liquid Plumr, Clorox	245	12.25	310	15.5	565	28.25
30	Liquid Plumr, Clorox	238	11.9	300	15	560	28

As shown from Table 50, the above tested commercial products contain a certain amount of sodium hydroxide or another strong base that require from 180 to 250 mL/L of acid to neutralize. The quantity of acid required to initiate chlorine release is approximately to the same as the quantity of acid required to reach pH=7; except Liquid Plumr. In case of Liquid Plumr, approximately 20%

more acid is required for initiation of chlorine release. This is most likely caused by the complicated composition of the Liquid Plumr product; it includes additives such as surfactants and viscosity regulators. As follows from Table 50, tested hypochlorite-based products are relatively stable in case of accidental mixing with a small quantity of acid, however, the addition of acid beyond the neutralization point (as listed in the third column of table 50), will result in the release of dangerous chlorine gas.

Prolonged storage of a NaClO based product or keeping its container open for a long time will result in a reaction of NaOH present in the product with CO_2 from the air. As a result, the product will lose its stability, so a smaller quantity of acid could be required for chlorine release initiation.

Accidental mixing of sodium hypochlorite product with an approximately equal quantity of acid or acidic cleaner will result in heating, foaming and extremely hazardous chlorine release.

Table 51 below represents the timing of real case scenarios involving tested commercial liquid hypochlorite products. Each product (50 mL) was combined with the equal volume (50 mL) of 10% HCl at the beginning of the experiment. The chlorine release happened immediately after the acid addition because the quantity of acid was in excess of what was required for neutralization and complete decomposition of NaClO in products. The chlorine release intensity is strongly dependent on the temperature and stirring speed. Columns 3 to 6 in table 51 represent an approximate time to reach 95% of maximum actual chlorine release from the three liquid hypochlorite products tested in this study at various mixing speeds and 3 initial temperatures. In the last two columns, chlorine concentration (mol Cl_2 gas per 1 liter of a product) and volume of released chlorine gas (liters of Cl_2 gas at 22 °C and atmospheric pressure released from 1 liter of a product) corresponding to 95% of maximum chlorine release for reference was recorded.

Table 51. Time to 95% of maximum Cl2 release from the HCl injection moment

Temp. °C	Product	Time to 95% Cl_2 release, min				95% chlorine release level, mol/L	95% chlorine release volume, L/L
		0 rpm	50 rpm	100 rpm	300 rpm		
15	Ultra San, ECOLAB	32.0	23.3	14.5	5.3	1.207	29.23
22	Ultra San, ECOLAB	19.5	13.2	7.4	2.5	1.249	30.25
30	Ultra San, ECOLAB	12.5	8.2	4.3	1.7	1.315	31.85
15	Javel 12, by SANY	25.7	19.6	12.0	4.1	1.085	26.28
22	Javel 12, by SANY	18.6	14.7	7.4	3.2	1.129	27.34
30	Javel 12, by SANY	12.6	9.5	4.5	2.0	1.191	28.84
15	Liquid Plumr, Clorox	165.5	53.6	34.8	8.1	0.556	13.47
22	Liquid Plumr, Clorox	138.6	45.2	26.5	4.7	0.587	14.22
30	Liquid Plumr, Clorox	118.3	31.1	10.7	1.2	0.618	14.97

As illustrated in the table above, the temperature and mixing accelerate the release of chlorine. These dependencies are especially strong in case of Liquid Plumr. The most dangerous situation could arise when intensely mixing liquid hypochlorite product with an acid at an elevated temperature. Then most of the chlorine gas will be released in a matter of a minute. A viscous sodium hypochlorite based products such as Liquid Plumr, if not stirred intensely, can react with acid for a period of more than two hours while releasing a hazardous amount of chlorine.

At elevated temperature and intensive mixing the initial chlorine release rate could reach 12 liters of chlorine (0.5 $mol \cdot L^{-1} \cdot s^{-1}$) per second from one liter of sodium hypochlorite based product. If this happened in a small closed space, then it could be a potentially fatal poisoning. In table 52, the initial rate of chlorine release from tested liquid products mixed with 10% hydrochloric acid at different temperatures and mixing speeds are summarized:

Table 52. Initial chlorine release rates from tested products, mixed with 10% hydrochloric acid at different temperatures and mixing speeds

Product	**Temperature °C**	**Mixing speed, rpm**			
		0	50	100	300
JAVEL-12	15	8.77E-04	6.18E-03	2.75E-02	1.05E-01
	22	2.25E-03	3.70E-03	2.62E-02	1.42E-01
	30	2.05E-03	3.88E-03	5.85E-02	1.78E-01
Ultra San	15	6.53E-03	6.75E-03	2.38E-02	9.13E-02
	22	1.17E-03	4.02E-03	6.05E-02	1.20E-01
	30	3.52E-03	8.87E-03	6.90E-02	1.52E-01
Liquid Plumr	15	4.12E-04	8.08E-04	1.60E-03	1.02E-02
	22	6.50E-05	4.93E-04	2.20E-03	1.28E-02
	30	1.19E-04	4.68E-04	4.50E-03	2.33E-02
		Rate of chlorine release, $mol \cdot L^{-1} \cdot s^{-1}$			

6.2 Solid hypochlorite products

Mixing of calcium hypochlorite, trichloro-s-triazinetrione or Sodium dichloro-s-triazinetrione dihydrate with a small or large volume of water did not result in fast chlorine release and is relatively safe. The hazardous chlorine concentration could however accumulate in a room with poor ventilation or in a closed container over a long period of time. For example, chlorine release levels accounted for one hour based on rates for 22 °C (Table 53) are 8.93E-03 mol for trichloro-s-triazinetrione and 1.04E-03 mol for Sodium dichloro-s-triazinetrione dihydrate. Calcium hypochlorite appeared to be the least reactive. However, all tested solid products are highly toxic and are active compounds that contain a lot of active chlorine. These solid products can violently react with compounds and products other than water, so they may not be considered as 100% safe.

The chlorine release rate from solid products decreases in the series from left to right:

Trichloro-S-Triazinetrione > Sodium dichloro-s-triazinetrione dihydrate > calcium hypochlorite

Summarized in the table below are initial chlorine release rates from tested products (active compound named), mixed with water at different temperatures and mixing speeds:

Table 53. Initial chlorine release rates from tested products, mixed with water at different temperatures and mixing speeds

Product	Temperature °C	Mixing speed, rpm			
		0	50	100	300
Trichloro-S-Triazinetrione	15	6.98E-07	7.87E-07	8.43E-07	9.65E-07
	22	1.88E-06	2.03E-06	2.30E-06	2.48E-06
	30	3.15E-06	3.32E-06	3.48E-06	3.72E-06
Sodium Dichloro-s-triazinetrione dihydrate	15	3.38E-07	2.50E-07	3.83E-07	4.07E-07
	22	2.18E-07	2.37E-07	2.78E-07	2.90E-07
	30	4.65E-07	4.88E-07	5.02E-07	5.83E-07
Calcium Hypochlorite	15	5.67E-09	6.83E-09	2.33E-09	1.16E-09
	22	1.42E-09	3.40E-09	2.15E-09	7.25E-09
	30	5.60E-10	1.06E-08	1.85E-08	2.98E-08
		Rate of chlorine release, mol · kg^{-1} · s^{-1}			

7. Future Work and Recommendations

This project studied reactions of solid hypochlorites with water. It was found that chlorine release rates from solid products are very low and in some cases, not detectable. However, those were reactions with water. From the structure and nature of those 3 types of hypochlorite products studied here, it is expected that they will violently react or even explode in the presence of organic materials, reducing agents and acids, such as hydrochloric acid:

$$Ca(ClO)_2 + 4HCl \rightarrow CaCl_2 + 2Cl_2\uparrow + 2H_2O \qquad (6)$$

$$C_3Cl_3N_3O_3 + 3HCl \rightarrow C_3H_3N_3O_3 + 3Cl_2\uparrow \qquad (7)$$

A shared recommendation is to test solid hypochlorite product’s reactivity with one another, other chemicals and products that are used for pool maintenance. We recommend this because the mixing of those products together is quite probable. A number of toxic and dangerous compounds may be formed as products of such reactions that could pose a toxic inhalation danger for product users. Calcium hypochlorite in presence of water can explosively react with trichloro-s-triazinetrione (Long, 2008). In addition, the study of reactions of solid products with hydrochloric acid could be a very logical addition to the present project.

The other danger that hypochlorites may cause in a household environment is in the formation of volatile and toxic chloramines. It is known that some of them have explosive properties (Okada, Akiyoshi, Ishizaki, Sato, & Matsunaga, 2014). Chloramines such as NCl_3, $NHCl_2$, and NH_2Cl could be formed from hypochlorites in presence of ammonia or salts of ammonium, the latter is present in a number of cleaners, dishwashing liquids polishers and similar products.

Bibliography

(2017). *Pamphlet 96 Sodium Hypochlorite Manual.* The Chlorine Institute.

Administration, O. S. (n.d.). *OSHA Method ID-126SGX Chlorine and Chlorine Dioxide in Workplace Atmospheres*. Retrieved from US Department of Labor: https://www.osha.gov/dts/sltc/methods/inorganic/t-id126sgx-pv-01-0112-m/t-id126sgx-pv-01-0112-m.html

Bjarnason, S. (2004). *Long-term Sequelae From Acute Exposure to Chlorine Gas: A Review* . Defence R&D Canada – Suffield .

Canada, T. (2017). *T8080-170164 Chlorine Release Project.*

Chase, M. J. (1998). NIST-JANAF Themochemical Tables, Fourth Edition,. *J. Phys. Chem. Ref. Data, Monograph 9*(1-1951.).

Gilchrist, H. a. (1933). The residual effects of warfare gases: the use of . *9 , 229-270.* .

Long, T. T. (2008). Explosion Risk from Swimming Pool Chlorinators and Review of Chlorine Toxicity. *Journal of Toxicology: Clinical Toxicology*, 33:4, 349-354.

Okada, K., Akiyoshi, M., Ishizaki, K., Sato, H., & Matsunaga, T. (2014). Analysis of an explosion accident of nitrogen trichloride in a waste liquid containing ammonium ion and platinum black. *Journal of Hazardous Materials*, 75-81.

Vallance, C. (2017). *An Introduction to Chemical Kinetics.* Morgan & Claypool Publishers.

William A. Rutala, P. M. (n.d.). *Guideline for Disinfection and Sterilization* .

Appendix 1. Chemical Kinetics Background

This information explains terms and considerations used in the kinetic study of the present project and intended to help readers understand experimental results avoid ambiguities.

“Reaction rate” or “Speed of reaction” is the speed at which chemical reaction proceeds. Both terms “Speed of reaction” and “Reaction rate” have the same meaning and both equally used in kinetic chemistry and physical chemistry depending on author’s preference.

The reaction rate could be expressed as consumption of a certain amount of a reactant during a unit of time or formation of an amount of a product during a unit of time. The reaction rate in “amount” or “quantity” units (per unit time) could be also expressed in terms of “concentration” units per unit time because concentration is an amount per unit of volume. Concentration is a relative term and could be more comfortable for use in practical applications. However, there are the cases where might be used only one of those two parameters.

Example (1): 1 kg of carbon (coil) is burned completely within one hour. The rate of reaction is -1 kg/hr accounted by carbon. According to the reaction equation, the other reactant is oxygen and the product is carbon dioxide:

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

It is possible to calculate the rate of the same reaction accounted for oxygen (O_2) and the product carbon dioxide:

1 kg of carbon = 32/12 kg of oxygen = 2.66 kg of oxygen (32 is the molecular weight (MW) of oxygen and 12 is MW of carbon). Accordingly, the rate of reaction (1) is -2.66 kg O_2/hr for oxygen.

For the carbon dioxide the rate will be: +44/12 kg/hr = +3.66 kg CO_2/hr. (44 is the MW of CO_2, and 12 is the MW of C). Note that rates for carbon and oxygen are negative, because they consumed in the reaction, but rate of CO_2 is positive because it is the product. As a result, the rate of reaction (1) has three numerically different values: -1kg C/hr = -2.66 kg O_2/hr = +3.66 kg CO_2/hr. In fact, it is the same rate of reaction but accounted for different reactants or product.

Example 1 represents average rate of reaction, and it was defined as the rate of a reaction over a predefined period of time. The time in this example is very important because if the predefined period of time will be different, the result will be also different. E.g. as for the day (24 hr period) each rate of reaction (1) will be lower in 24 times.

The same is true for rate of reaction expressed in terms of concentration. This is more applicable to chemical reactions conducted in gas or liquid phases.

In general rate of reaction can be expressed as a change of concentration (Δconcentration) of any of reactants or products of a reaction per unit of time (Δtime):

$$\text{Rate} = \Delta\text{concentration}/\Delta\text{time} \quad (2)$$

Example (2): A product "Ultrasan", tested within the project T8080-170164, was reacted with HCl and chlorine gas released as a product of sodium hypochlorite decomposition:

$$NaOCl + 2HCl \rightarrow Cl_2\uparrow + NaCl + H_2O \quad (3)$$

As measured in the experiment, the total amount of chlorine released from Ultrasan product at 15°C upon complete consumption of reactants was 1.27 Mol/L (see Table 10 in the report, first line, and fourth column). We also know that reaction completed before 1 hr period (see Fig.1 below). Same as in example (1) we may determine the average rate for the 1 hr period:

Rate = 1.27 Mol Cl_2/hr = 0.02117 Mol Cl_2/min = 0.000353 Mol Cl_2/s

However at the time 10 min was already registered the same amount of chlorine (see Fig.1 below) and for the 10-minute period the rate shall be calculated as 1.27 Mol Cl_2/10 min = 0.127 Mol Cl_2/min = 0.002117 Mol Cl_2/s. Please note, the rate calculated for 10 min is 6 times higher than for one hour.

Most reactions slow down as the reactants are consumed. Consequently, the rate given by the expression (2) shown above tend to lose its meaning when measured over longer time intervals Δt. In this sense average rate of reactions calculated for pre-determined period is not very informative.

In the example (2) experiment has been recorded amount of the released chlorine over the time period as a data set (Cl_2 concentration measured every 0.1 seconds) which forms a virtually continuous curve as it presented below:

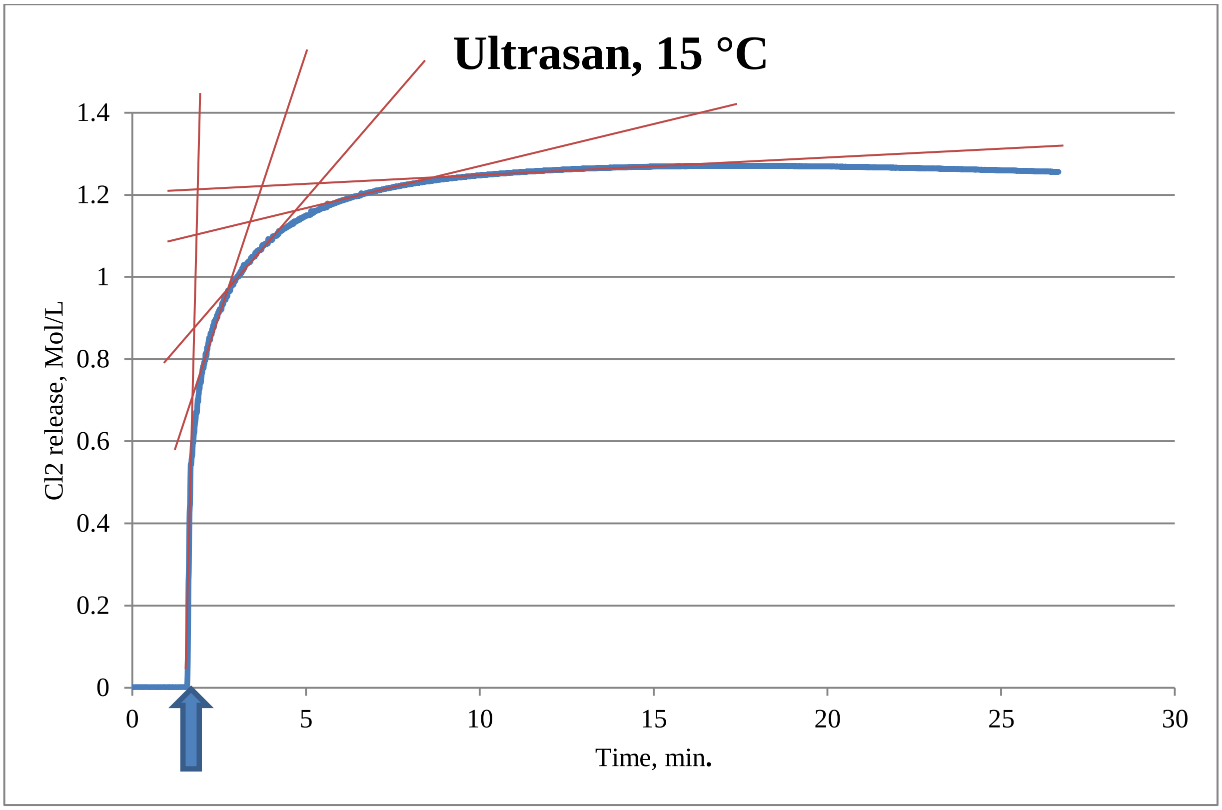


Fig. 1. *Chlorine release from Ultra San product reacted with 10% HCl at 15 °C. The arrow shows time point where HCl was injected (reaction start).The thin red lines are tangent lines to the chlorine release curve at certain time points.*

Based on Fig. 1, one could see the reaction is completed at the experiment time of about 10 minutes as no more chlorine release was detected and the chlorine release curve becomes horizontal (or forms the plateau).

Fig. 1 above is very informative because it provides information to calculate the rate of reaction at any specific time points by drawing tangent lines at the point of interest, as illustrated on the figure. The reaction rate can be calculated as the slope of the tangent line (remember a line equation: Y = M · X + B, so the "M" parameter is the reaction rate). This could be done graphically, but much more precisely one can calculate rate using the following equation:

$$rate = \frac{[Cl2\ at\ t2]-[Cl2\ at\ t1]}{t2-t1} \qquad (4)$$

Equation (4) could be also expressed as follows:

$$rate = \frac{\Delta[Cl2]}{\Delta t} \qquad (5)$$

As mentioned, Fig.1 represents computer data set acquired with high frequency, in total it consists of 36,000 individual high-resolution measurements of chlorine concentration and this allows calculation of Instantaneous rates of reaction at any of 36,000 single time point. The instrument acquisition software could be set to almost any frequency, such as 1000 Hz will result in 1000 measurements per second and the total number of points will be 3,600,000. This means that the time interval Δt at which rate is calculated could be chosen smaller and smaller until it becomes almost indefinitely small, comparing to the whole curve. The instantaneous rate could be expressed as:

$$rate = \lim_{\Delta t \to 0} \frac{\Delta[Cl2]}{\Delta t} \qquad (6)$$

Due to a very high acquisition rate this equation becomes differential:

$$rate = \frac{d[Cl2]}{dt} \qquad (7)$$

In other words the instantaneous rate of reaction is the first derivative of concentration over time:

$$Inst.\ rate = \lim_{\Delta t \to 0} \frac{\Delta[Cl2]}{\Delta t} = \frac{d[Cl2]}{dt} = [\mathrm{Cl}_2]' \qquad (8)$$

For the example (2) values of $\frac{d[Cl2]}{dt}$ (the first derivative of concentration) have been calculated for each data point; the result is presented below (Fig.2).

Again, the term “Instantaneous rate” refers to the whole curve in the Fig. 2 starting from the blue arrow (from the acid injection moment).

As shown in Fig. 2, the instantaneous rate has the maximum at about reaction initial time (acid injection moment), then goes lower and also it has a lot of variabilities, quickly alternating between positive and negative values and after a certain time becomes equal to zero. One can expect rather high rate at the beginning of a reaction and zero rate at the end. The negative “pulses” on the instantaneous rate show dependence of this rate on random factors, in this particular example a “positive pulse” occurs when one or several bubbles of chlorine pop-up from the liquid phase creating sudden rise in chlorine concentration in the gas phase which is immediately registered by the detector; the “negative pulse” occurs when no bubbles pop-up for some time and the chlorine from previous pop-ups being mixed with the rest of the gas phase in the setup and as a result the detector records a bit lower concentration comparing to the “pop-up” time point. The small but sudden drops in chlorine concentration result in the deep negative “pulses” on the instantaneous rate curve.

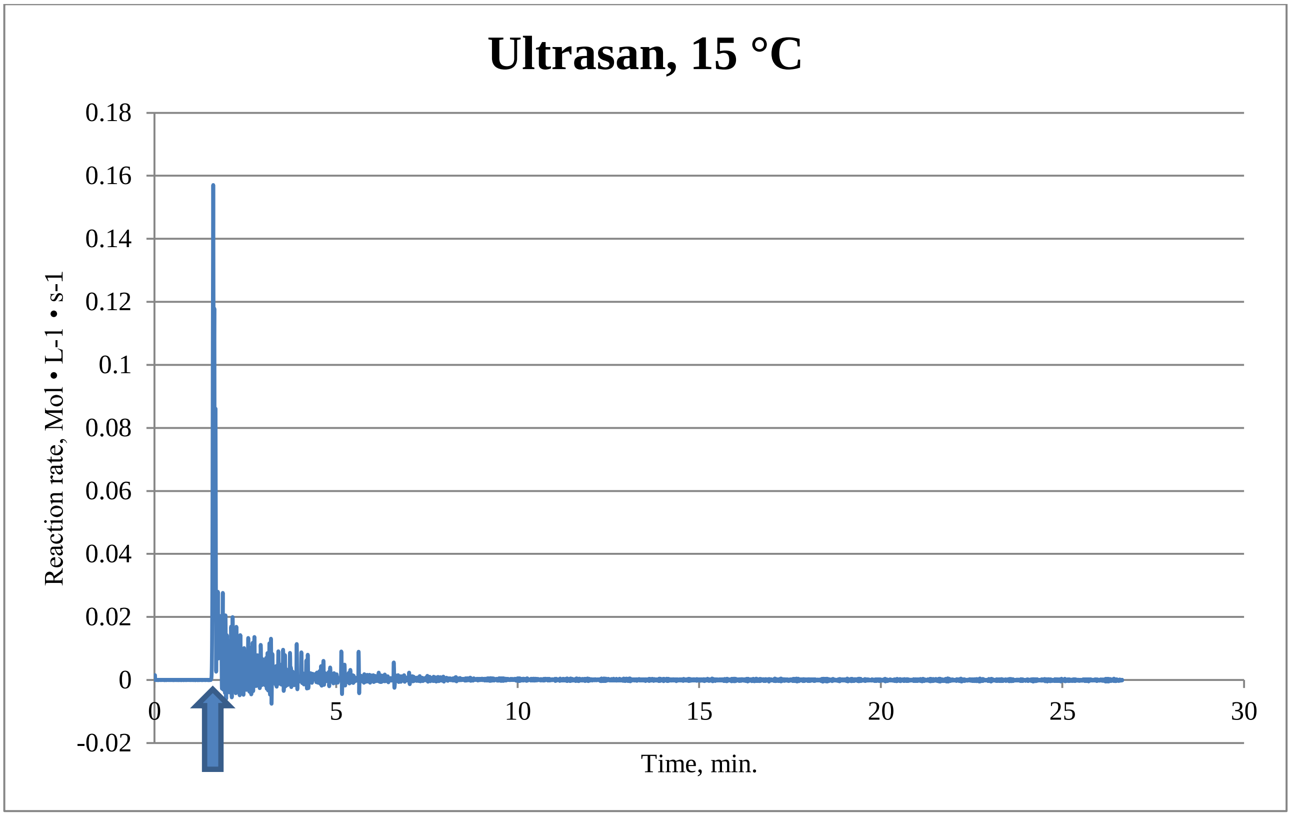


Fig. 2. *Instantaneous rate of chlorine release from Ultra San product reacted with HCl at 15 °C The arrow shows time point where HCl was injected (reaction start).*

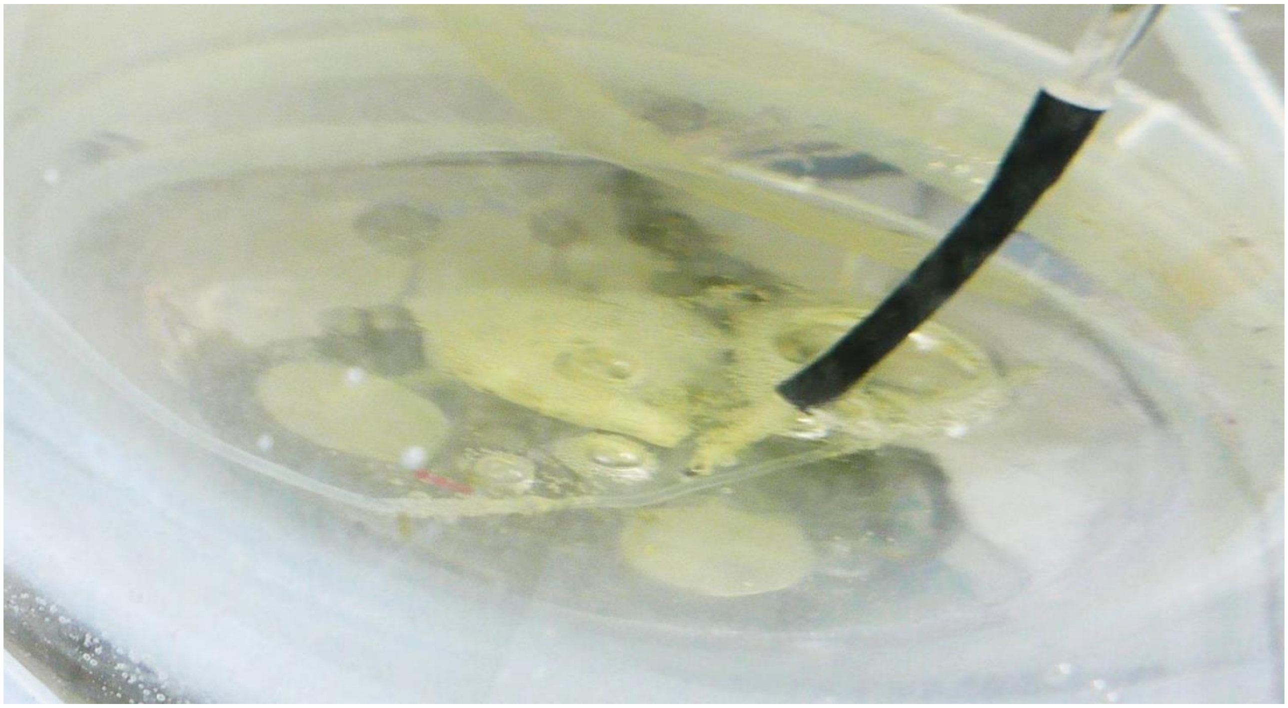


Fig. 3. *Picture of the reactor during reaction of Ultrasan product with HCl; Clearly visible large (behind the temperature sensor) and small bubbles of chlorine on the surface of the reaction mixture.*

Other random factors also can influence the instantaneous rate such as vibrations, pump phase, pump speed variation and so one. Please note that those factors influence chlorine release rate from the liquid phase as it is registered by the detector. A reaction conducted in theoretical “ideal” conditions may have no such positive and negative “pulses”.

To calculate kinetic parameters of a reaction (Arrhenius parameters) required so-called “initial rate” of chlorine release. The initial rate is the rate of a reaction at the so-called time zero (t=0). The t=0 is defined as a moment when reactants completely mixed together at their higher concentration and as a result, the reaction rate is at its maximum. Typically, kinetic chemistry textbooks demonstrate the initial rate and the t=0 using an ideal “theoretical” plot where t=0 is located on the time axis at the time zero. However, this never happens in experimental conditions, even if reactants are pre-mixed and reaction initiated by a spark or light flash (a flash photolysis experiment). A close experimental approximation to the “ideal” textbook conditions is possible in case of a slow reaction when mixing of reactants takes an indefinitely small part of the time, needed for the reaction to be completed. A good example of this is reactions of solid hypochlorite products with water.

In the example (2) experiment the t=0 is not the first data point because during the first minute the zero baseline is recorded and no reaction happened. t=0 is not the moment of the acid injection because injection is a period (in this example it takes 1.2 seconds). At the beginning of the acid injection the reaction has not yet begun; at the end of injection the reactants may not be completely mixed yet. According to the t=0 definition, t=0 shall be located sometime after the end of the acid injection. Since the reaction rate is a function of concentrations of reactants each into the other, the maximum of the reaction rate is the indication of t=0 position. Practically, the kinetic chemist shall choose a small region on the concentration curve, where the reaction rate reaches its maximum. The reaction rate maximum is located on the concentration curve just above the blue arrow shown in the Fig. 1. Fig. 4 represents the magnified area of the concentration curve above that blue arrow in the Fig. 1. A small (a few data points) region as shown in Fig.4 shall be used for calculation of the tangent line parameters (the red line in the Fig. 4). Normally least square linear regression method is used for the tangent line parameters calculation. The slope of the tangent line corresponds to the "apparent" initial reaction rate, required for further Arrhenius' calculations and in fact, it shows the position of t=0 which is the point of intersection of the tangent and the x-axis:

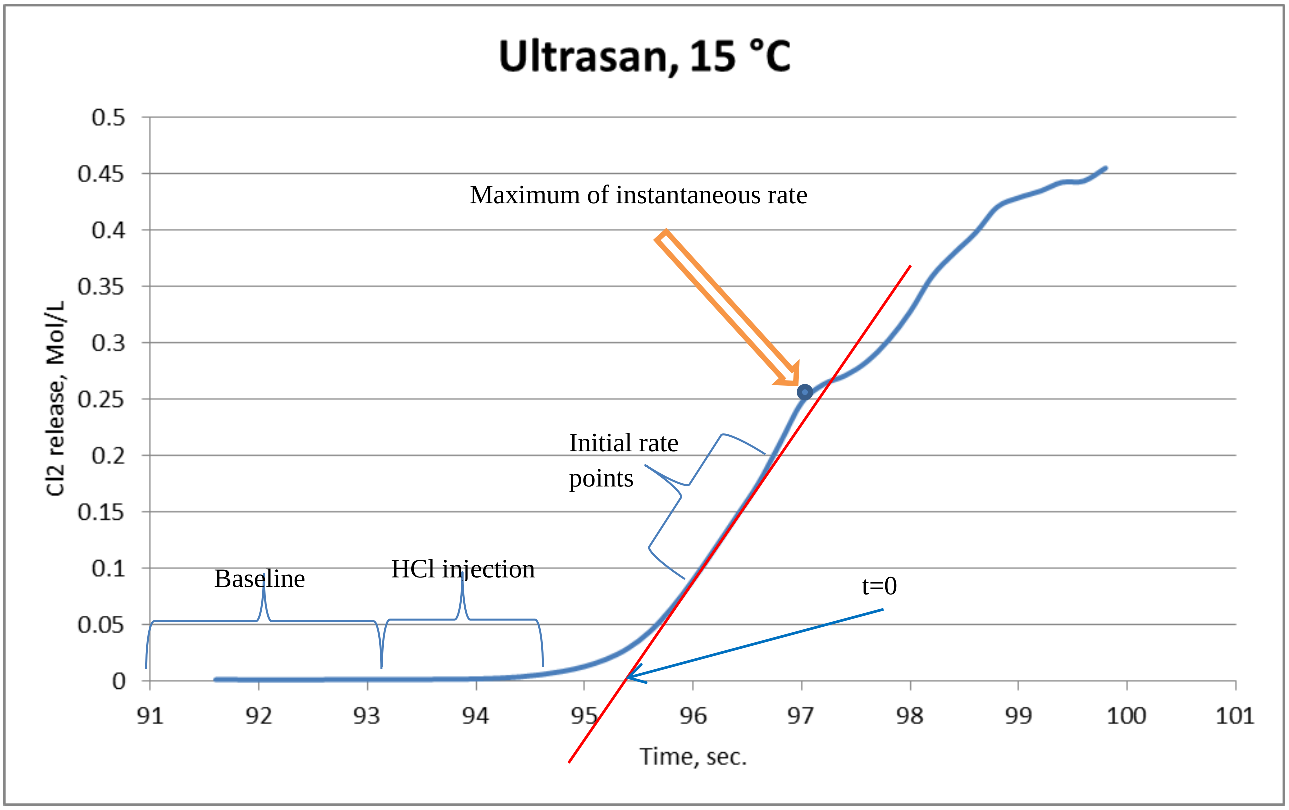


Fig. 4. *Chlorine release from Ultra San product reacted with HCl at 15 °C; part used for initial rate calculation.*

Please note, in case of no mixing, or poor mixing and a high viscosity of reactants, the "initial time" region could be located at a much later part of the concentration curve, or it may not exist at all if the reactants did not mix completely over the period of the experiment. In such situation, the reaction rate is controlled by diffusion of reactants from one layer into another, but not by thermodynamics, this observed in experiments with Liquid Plumr.

In Fig. 4 one can see an orange arrow which points to a "bump" on the concentration curve. This point is important because at this exact moment the first derivative (which is the instantaneous chlorine release rate) reaches its maximum. This point is easy to find and process without manual selection of data points, as was required for determination of the “initial” reaction rate. Please note, the instantaneous rate is the whole curve as on the Fig.2, however, the “maximal instantaneous rate” is just one point where this curve reaches its maximum. There must be some difference in initial and “maximal instantaneous” rates because of a number of random factors that influence instantaneous rate, and normally the value of “maximal instantaneous rate” is slightly higher than the “initial” rate, but both of them suitable for Arrhenius parameters calculations.

Both instantaneous and maximal initial rates were reported for this study as rate constants ($Mol \cdot L^{-1} \cdot s^{-1}$) for each product, temperature and mixing speed.

Temperature Dependence - Arrhenius parameters

Rates of chemical reaction generally depend on temperature, in most cases the reaction rate increases with an increase of the temperature. This happens because as the temperature increase, the kinetic energy of the reactants increases, allowing for more collisions between the molecules. This, therefore, allows for products to be formed faster. In case of chlorine gas release from liquid reactant mixture the temperature also influences the solubility of chlorine allowing quicker evaporation at increased temperature. The equation describing dependency of reaction rate on temperature was proposed by Svante Arrhenius in 1889 and since then this formula is one of the most important tools in chemical kinetics. This equation allows prediction of reaction rate at any temperature, and it is applicable to reactions that could be conducted both in a “clean” near ideal condition and to reactions kinetics that are complicated by phase-transfer, diffusion, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions.

Arrhenius' equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature (T), a pre-exponential factor (A), energy of activation (E_a) of the reaction and universal gas constant R ($R = 8.314 \frac{J}{mol\ K}$):

$$k = A \times e^{\frac{-Ea}{RT}} \qquad (9)$$

The goal of the kinetic study is to determine the activation energy E_a of the reaction and pre-exponential factor A. To do so minimum two experiments are required where the reaction rate could be determined at two different temperatures. Three and more temperature points would allow to increase the accuracy of a kinetic study. To calculate activation energy E_a and pre-exponential factor (A) we need to rearrange the Arrhenius' equation in the strait-line format:

$$k = A \times e^{\frac{-Ea}{RT}} \qquad \rightarrow \qquad Ln\ k = \left(-\frac{Ea}{R}\right) \times \left(\frac{1}{T}\right) + \ln\ A \qquad (10)$$

The formula of the straight line is Y = M·X + B, so the re-arranged Arrhenius' equation could be plotted as a straight line in coordinates Y → ln k and $X \rightarrow \frac{1}{T}$. The data points (ln k vs. 1/T) will result in a straight line. Of course minimum two points required to define a line. As a result we may determine the line parameters M which is the line slope and it is = -Ea/R; and B which is = lnA:

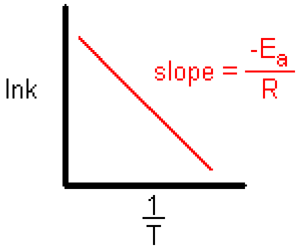


Fig. 5. Example of Arrhenius' plot

It is rare when the plot is required to calculate E_a and A, for example here is the formula for calculation of E_a for two points (k1 – T1 and k2 – T2):

$$Ea = \frac{R\, ln\frac{k2}{k1}}{\frac{1}{T1} - \frac{1}{T2}} \qquad (11)$$

In case of three or more data points as shown in the table below,

T, K	K, Mol/L s	1/T	lnk
288.15	0.0914	0.00347	-2.39251
295.15	0.12	0.003388	-2.12026
303.15	0.1521	0.003299	-1.88322

the least square linear regression method should be used, and the resulting graph is presented in Fig. 6 below:

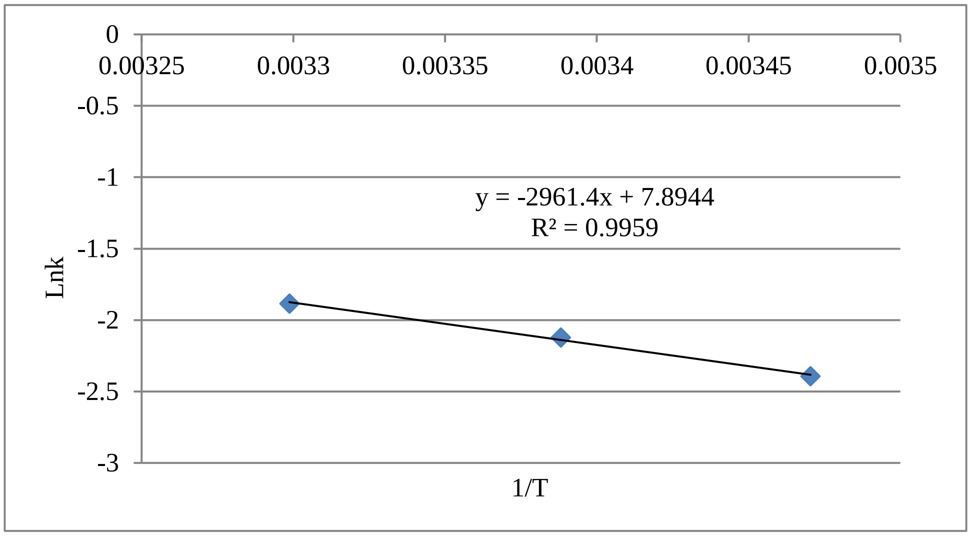


Fig. 6. *Arrhenius plot for Initial max. kinetic parameters, Ultra San product.*

On the plot above one can see three data points obtained in three experiments at three different temperatures (15, 22, and 30 °C). The black line on the plot is the result of the least square linear regression calculated by the computer. The numerical result of the regression presented in this figure as a straight line equation (y=M·x+B) with parameters M= -2961.4 and B=7.8944. The parameter R^2 on the plot is the regression linear fit (a statistical parameter, a square of the sample correlation coefficient; it equals to 1 if the fit is perfect and equals to 0 if there is no fit; the value of R2=0.9959 means that we did experiments with a great accuracy). Accordingly, E_a was calculated as follows:

$$Ea = -\frac{M}{R} = -\frac{(-2961.4)}{8.314\frac{J}{mol\,K}} = 24.61\ \mathrm{kJ/Mol} \qquad (12)$$

The pre-exponential factor (A) can be calculated as follows:

$$A = e^{B} = \exp(7.8944) = 2680\ s^{-1} \qquad (13)$$

The kinetic parameters for the reaction of hypochlorite products with HCl or water for this study was calculated and reported as described above.

From the practical point of view the Arrhenius' equation gives possibility to predict reaction rate at any temperature. The Arrhenius' equation is based on thermodynamic laws; E_a corresponds to the energetic barrier that a molecule need overpass in order for reaction to happen. If the E_a is high, then the reaction could be slow, however, it has a strong dependence on the temperature. Low E_a means the reaction has low temperature dependence and reaction is fast. All catalysts increase reaction rate by lowering Ea. Thermodynamically, E_a may not be negative; however there are a lot of processes that slow down as the temperature rises, and mathematically E_a could have a negative value. The negative E_a implies that the process is complicated and not controlled by thermodynamics; instead it may have diffusion, mixing, mobility or other rate limitations.

Pre-exponential factor A is also important as it relates to collision frequency, i.e. a number of collisions of reactants can be not successful because of steric geometrical factors. Therefore the rate of a reaction is proportional to the A parameter directly.

Appendix 2: Iodometric Titration Procedure for Determination of Hypochlorite

Numerous methods are based upon the oxidizing-reducing properties of iodide ion:

$$2\,I^{-} - 2\,e^{-} \rightarrow I_2$$

$$I_2 + 2\,e^{-} \rightarrow 2\,I^{-}$$

Iodine, the reaction product, is ordinary titrated with a standard sodium thiosulfate solution, with starch serving as the indicator (or platinum redox electrodes could be used):

$$I_2 + 2Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6$$

Primary standard is potassium iodate: Iodate (IO_3^{-}) reacts with an excess of iodide in acid solution to yield triiodide (equivalent of I_2), which is subsequently titrated with the standardized thiosulfate solution.

$$IO_3^{-} + 8I^{-} + 6\,H^{+} = 3\,I_3^{-} + 3\,H_2O$$

Apparatus

1.5- or 2-L beakers

1-L storage bottle

250-mL Erlenmeyer flasks, three

10-mL graduated cylinder

2-mL pipette

50-mL burette

Burners and tripods

Chemicals

Hydrochloric acid (6 M) (~22%)

Potassium iodate

Potassium iodide

Sodium carbonate

Sodium thiosulfate pentahydrate

Soluble potato starch

Sulphuric acid (3 M)

Preparation of Standard Sodium Thiosulfate Solution

1. Dissolve approximately 0.1 g of sodium carbonate in one liter of distilled water. The sodium carbonate is added to adjust the pH of the solution to about 9 or 10. Dry the primary standard KIO3 at 110 °C for 1 hr or confirm that it has already been dried.

2. Prepare a 0.1-M thiosulfate solution by dissolving approximately 25 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$; FW 248.19) in the sodium carbonate solution.

Transfer the solution to a clean storage bottle, and store the solution in the dark.

3. The next three steps involve preparation of the indicator. Prepare a paste by adding about 2 g of soluble starch to 30 mL of deionized water. The starch serves as the indicator for titrations involving iodine.

4. Boil about 1 liter of water in a 1.5- or 2-L beaker and add the paste. Stir the solution while continuing to heat until the solution is completely transparent. If the solution remains cloudy after at least 15 min of heating, continue to step 5. The solution is still usable.

5. Cool the starch indicator solution and place it in a clean storage bottle (LABEL IT!).

6. Fill a 50-mL burette with the thiosulfate solution.

7. Weigh to ± 0.1 g approximately 2 g of reagent-grade potassium iodide into each of three numbered 250-mL Erlenmeyer flasks. Add 25 mL of water and 2 mL of 6 M hydrochloric acid to each flask. Swirl the solution to dissolve the potassium iodide.

8. Number three weighing bottles or three small beakers with the same numbers used for the Erlenmeyer flasks.

9. Into each weighing bottle or beaker weigh to the nearest 0.1 mg between 0.12 and 0.15 g of potassium iodate (FW 214.00). Record the mass of the potassium iodate in each container.

10. Add the potassium iodate in one of the numbered containers to the solution in the identically numbered Erlenmeyer flask. Rinse in any remaining particles with a small amount of water. Swirl the solution to dissolve the potassium iodate. The brown color of triiodide should be apparent in the mixed solution.

11. Titrate the solution in the Erlenmeyer flask with the thiosulfate solution until the triiodide color has become noticeably less intense. Add 5 mL of the starch indicator and continue the titration until the dark-blue color of the starch-triiodide complex just disappears. Record the endpoint volume to the nearest 0.01 mL, and use fractional drops if necessary.

12. Individually repeat steps 10 and 11 with the remaining two potassium iodate samples. To minimize error, generate the triiodide just before you titrate it with thiosulfate.

13. Make zero sample (no potassium iodate added) titrate it and subtract from previous results for potassium iodate.

Calculations - Preparation of Standard Sodium Thiosulfate Solution

Molarity of Sodium Thiosulfate Solution:

$[Na_2S_2O_3] = 6 * 1000 * \text{mass of KIO} / 214 / \text{vol } Na_2S_2O_3$

Iodometric Determination of Hypochlorite in Commercial Bleach Product

In most liquid laundry bleaches and in some solid bleaches, the active ingredient is hypochlorite (OCl^-). Liquid bleaches usually contain sodium hypochlorite and the bleaching action is caused by the strong oxidizing properties of OCl^-, which also are exploited in this iodometric determination of hypochlorite. In the experiment, iodide is used to reduce the hypochlorite in bleach. The reaction in acid solution yields chloride and triiodide.

$$OCl^- + 3I^- + 2H^+ = Cl^- + I_3^- + H_2O$$

The triiodide formed in this reaction is titrated with the standard thiosulfate solution that was prepared earlier.

$$2 S_2O_3^{2-} + I_3^- = S_4O_6^{2-} + 3I^-$$

The endpoint of the titration is located with the starch indicator solution that was also prepared earlier.

1. Add 50 mL of deionized water and between 1.5 and 2.0 g of potassium iodide to each of three 250-mL Erlenmeyer flasks. Stir the solutions until the potassium iodide in each flask is dissolved.

2. Add 10 mL of 3-M sulfuric acid to each flask.

3. Use a pipette to place exactly 2.00 mL of liquid bleach (or 0.2000 g of dry product) into one of the flasks, and stir by swirling the solution. Fill a 50-mL burette with standard sodium thiosulfate solution, and use the thiosulfate solution to titrate the triiodide formed during the reaction of bleach with iodide. When the triiodide color starts to fade, add 5 mL of starch solution and continue the titration to the endpoint. Record the endpoint volume to the nearest 0.01 mL.

4. Make zero sample titration and subtract zero sample result from unknown sample results.

Calculations of % of active compound in hypochlorite products:

First calculate amount of equivalent chlorine (Cl_2) per liter or per kg of product.

eq[Cl_2][Mol/L, Mol/kg] = [$Na_2S_2O_3$][Mol/L]*Vol($Na_2S_2O_3$)[mL]/vt(product)[g,mL]/2

NaClO solutions (Javel-12, Ultra San, Liquid Plumur):

MW of NaClO = 74.44;

% of NaClO = eq[Cl_2]*74.44/10 (One active chlorine per molecule = Cl_2)

$Ca(ClO)_2$:

MW $Ca(ClO)_2$ = 142.98

% of $Ca(ClO)_2$ = eq[Cl_2]*142.98/2/10 (Two active chlorines per molecule = $2Cl_2$)

Trichloroisocyanuric acid:

MW Trichloroisocyanuric acid = 232.4

% of Trichloroisocyanuric acid = eq[Cl_2]*232.4/3/10 (Tree active chlorines per molecule = $3Cl_2$)

Sodium dichloroisocyanurate dihydrate:

MW Sodium dichloroisocyanurate dihydrate = 255.971

% of Sodium dichloroisocyanurate dihydrate = eq[Cl_2]*255.971/2/10 (Two active chlorines per molecule = 2Cl2)

Iodometric titration results:		
Name of product	% ACTIVE compound	Name of active compound
NaCLO -15% - Sigma-Aldrich	15.002	NaClO
Javel 12, by SANY	10.448	NaClO
Liquid Plumr, Clorox	5.224	NaClO
Ultra San, ECOLAB	11.734	NaClO
Super Shock hth	83.746	$Ca(OCl)_2$
Stabilized chlorinating granules	91.22	Sodium dichloroisocyanurate dihydrate
Trichloroisocyanuric acid	93.04	Trichloroisocyanuric acid

Appendix 3. Techniques for chlorine gas analysis.

Chlorine analysis techniques overview and suitability for the study

In this project, an essential pre-requisite was a proper analytical technique suitable for chlorine gas quantification. There are a number of methods for chlorine analysis, based on different properties of chlorine. Chlorine is a strong oxidizer, and therefore it may be analyzed by common reduction-oxidation methods such as iodometric titration. However, this method deals with solutions, not gaseous chlorine, although chlorine gas can be initially dissolved in liquid and then analyzed. This is done in OSHA method ID-126SGX (OSHA), where air contaminated with chlorine gas is put in contact with 2% KI solution, and then the released iodine is titrated with sodium thiosulfate. Another popular method is the potentiometric method, where reduction-oxidation potential is measured in a solution using a platinum electrode. However, those two methods are not chlorine-specific, because they account not only for chlorine but for any oxidizer, such as ozone, nitrogen oxides, chlorine oxide etc. Also, they have a limited concentration range and again, the chlorine must be dissolved in solution, which is not suitable for a continuous gas analysis.

Chlorine is a reactive compound and it can be analyzed for example by discoloration of a dye, methyl orange, and the color change can be measured colorimetrically.

Chlorine can react with reducing agents and form chloride-ion Cl^-, which also can be analyzed, by methods such as, ion-selective potentiometry, or by the gravimetric analysis – chlorides can be precipitated with silver nitrate as AgCl. This is one of the oldest methods.

Finally, chlorine can be analyzed as is, without any reactions involved, just based on its physical properties. Chlorine can be relatively easily condensed or frozen in an ampule and then weighed; however, this has never been an analytical method because of enormous errors. Instead, there are other physical properties of chlorine that can be used for accurate analysis.

A gas mass spectrometer with electron impact ionization (Thermo Finnigan PolarisQ) can be and was used for chlorine analysis:

Fig.1. Thermo Finnigan PolarisQ mass spectrometer equipped with gas chromatograph and sample management and dilution system for chlorine analysis.

The air with chlorine from the reaction flask continuously passed into the mass spectrometer inlet through a deactivated fused silica capillary. A flow of gases enters ionization source of the mass spectrometer, is then ionized by an electron beam and is then separated and analyzed by mass-to-charge ratios. Chlorine produces several detectable ions: two isotopes 35 and 37 m/z and three molecular ions with m/z = 70, 72, and 74.

No other gas in the air can produce a similar mass spectrum, so chlorine was able to be quantified selectively and continuously, in real time. The analytical signal was electronic counts of chlorine ions over time, and it was suitable for processing with spectrometry and chromatography software, similar to a UV-Visible spectrophotometric signal. During this project, two disadvantages of this method have been found:

First, the mass spectrometer required dilution of the gas sample using an electronically controlled valve system and as a result analytical rate was not sufficient (1 measurement per 2 seconds). The second and a major disadvantage was the fact that the method is destructive by nature: the gas mixture to be analyzed is continuously consumed by the mass spectrometer. This affected the overall concentration of chlorine in the setup and caused problems with pressure in a closed setup. However, the mass spectrometry technique has been used for confirmation of spectrophotometry results.

UV-Visible Adsorption Spectroscopy

Another method, based on chlorine's very distinct UV-Visible adsorption spectrum was used for fast, real-time, accurate and sensitive quantitative analysis using UV-Vis spectrophotometer equipped with appropriate gas flow cell:

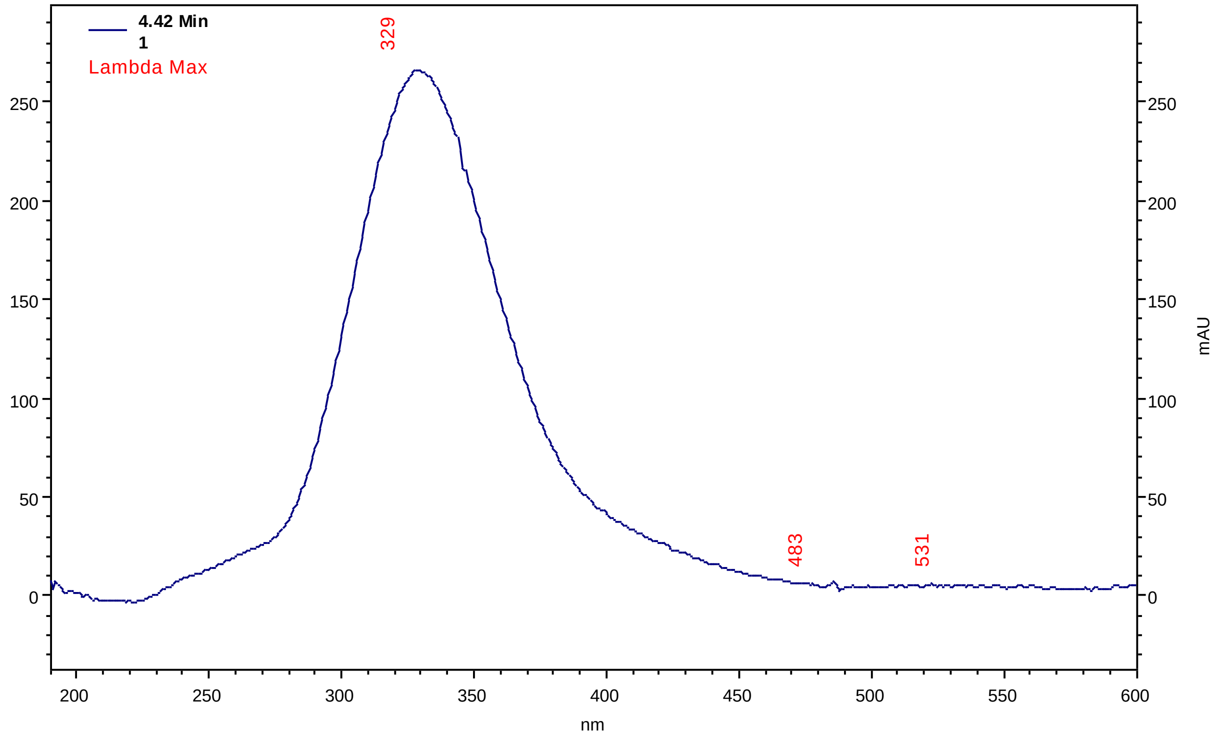


Fig. 2. UV-Vis Adsorption spectrum of chlorine in gas phase.

The spectrophotometric method was the best choice for the Chlorine Release Project because it provides very high accuracy, specificity, repeatability, sensitivity, broad range, and continuous real-time analysis. A very high measurement rate (20 or more high resolution measurements per second) makes this method ideal for kinetic experiments (measurement of reaction rates). Additionally, the spectrophotometric method is not destructive like all other methods mentioned above. This is very important since using non-destructive methodologies allow for the chlorine and other gases to not be consumed during the experiment; making this entire setup very accurate.

Appendix 4. Amount of water required for calcium hypochlorite titration

Within Task 1, solid calcium hypochlorite in a powder form was mixed with different predefined amounts of water at the beginning of each experiment and then the chlorine release was measured. The amount of added water was calculated based on one of the desired concentrations of $Ca(ClO)_2$ vs. H_2O: 60%, 75%, 80%, 85%, 90%, 95% and 99%. For each experiment, 50 g of $Ca(ClO)_2$ was placed into the reactor of the closed setup, the system was closed, data acquisition initiated and only then the required amount of water was added by injecting it inside of $Ca(ClO)_2$ powder through the Teflon capillary.

The amount of water required for calcium hypochlorite titration was calculated as follows:

$$Wt(H2O) = \frac{50g \ \times (100\% - [Ca(ClO)2]\%)}{[Ca(ClO)2]\%}$$

Where $Wt(H_2O)$ is the required amount of water in grams, 50g is the mass of $Ca(ClO)_2$ used in the experiment; $[Ca(ClO)_2]$ is the required concentration of $Ca(ClO)_2$.

The calculation results are summarized in the table below:

$Ca(ClO)_2$ concentration, %	60	75	80	85	90	95	99
Dry $Ca(ClO)_2$ mass, g	50	50	50	50	50	50	50
H_2O mass, g	33.33	16.67	12.50	8.82	5.56	2.63	0.51

For example, to make experiment with 60% $Ca(ClO)_2$, exactly 50 grams of dry $Ca(ClO)_2$ placed into the reactor, and then 33.33 grams of water added into the reactor.