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EXPERIMENTAL ANALYSIS OF RADIATION INDUCED CORROSION OF COPPER CANISTERS DESIGNED FOR KBS-3 A FINAL REPOSITORY FOR SPENT NUCLEAR FUEL

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Riassunto

Il seguente lavoro di tesi presenta il risultato dell'attività svolta durante il periodo di ricerca presso la facoltà di "Chimica e Ingegneria Chimica" del KTH, Kungliga Tekniska Högskolan, a Stoccolma, Svezia. La ricerca sperimentale qui presentata è stata portata a termine presso i laboratori della sezione di "Chimica Nucleare" della divisione di "Chimica Fisica Applicata".

Il principale progetto seguito dallo staff del laboratorio di ricerca della suddetta divisione riguarda i materiali utilizzati nel KBS − 3 concept, uno dei più avanzati progetti di deposito permanente di scorie nucleari ad alto livello di radioattività mai sviluppato.

Il suddetto modello per il deposito di scorie nucleari, denominato KBS − 3, viene progettato dalla società SKB (Swedish Nuclear Fuel and Waste Management Company) sin dal 1976 ed è ad oggi considerato la migliore e unica alternativa per lo stoccaggio permanente delle scorie radioattive in Svezia. Nel 2011 è stato definito il sito che ospiterà questo deposito che sarà nel comune di Östhammar, a 150 km a nord di Stoccolma, le richieste per il via libera alla costruzione di questo deposito sono state quindi inviate alle autorità competenti.

Il progetto KBS − 3 vuole tutelare l'ambiente dalla presenza di radionuclidi tramite l'utilizzo di un metodo cosiddetto a tre barriere. Queste barriere sono costituite da : un contenitore cilindrico in rame che incapsula le scorie sigillate, un materiale tamponante costituito da argilla bentonite ed infine come ultima barriera viene utilizzata la roccia granitica circostante.

Il progetto prevede la costruzione di tunnel sotterranei a una profondità di 500 metri sotto il livello del mare in cui vengono posizionati i barili contenenti le barre di combustibile esausto inserite in una anima di ghisa che è incapsulata da un rivestimento cilindrico di rame purissimo. Ciascun contenitore è quindi sotterrato in uno strato di argilla che protegge i barili di rame da molteplici processi corrosivi provenienti dall'esterno, ritarda la migrazione di radionuclidi e attenua le forze di pressione provocate da possibili scosse della roccia granitica. La scelta di un deposito geologico costruito a grandi profondità nel terreno è considerato la migliore soluzione adottabile, infatti lo strato roccioso del sottosuolo svedese è considerato stabile da migliaia di anni.

Le ricerche condotte per questo lavoro di tesi hanno lo scopo di valutare le proprietà di resistenza alla corrosione della prima barriera, cioè il contenitore di rame che incapsula le scorie ad alta radioattività. Esso deve essere in grado di rimanere stabile e integro per tutta la durata operativa del deposito e mantenere intatte le proprietà di resistenza alla corrosione esterna e di dissipamento del calore di decadimento.

Il modello descritto dall'SKB prevede che il deposito si mantenga stabile e resista a fenomeni corrosivi anche in presenza di future possibili ere glaciali per un periodo di tempo di circa 100 mila anni.

Studi condotti precedentemente a questo lavoro hanno messo in discussione l'integrità del contenitori cilindrici in rame durante questo lungo lasso di tempo di approssimativamente 100000 anni. Da questi studi sono emerse svariate cause di possibili processi corrosivi del contenitore di rame che non erano stati presi adeguatamente in considerazione, questi risultati mettono in discussione le capacità del canister di operare come barriera protettiva a lungo termine.

Da alcuni studi si evince che la superficie di rame metallico in condizioni anaerobiche esposta a possibili infiltrazioni d'acqua, che peraltro si cerca di evitare, subisce dei processi di corrosione attribuibili al fenomeno di irradiazione proveniente dal combustibile esausto.

Pur essendone stata dimostrata l'importanza, in letteratura sono disponibili pochissimi dati inerenti al fenomeno di corrosione del rame indotto da radiazione.

Il lavoro sperimentale di seguito presentato vuole apportare delucidazioni su questo fenomeno che è ancora poco investigato date le molteplici difficoltà nella rappresentazione in laboratorio delle condizioni a cui la superficie del rame è soggetta nel deposito.

Il fenomeno che vuole essere valutato è il processo di corrosione che avviene sulla superficie del contenitore di rame quando esso entra in contatto con infiltrazioni d'acqua che nel sottosuolo hanno proprietà anaerobiche. I processi di corrosione che vanno investigati coinvolgono le specie ossidanti prodotte dalla radiolisi dell'acqua che in contatto con la superficie metallica di rame ne destabilizzano la superficie.

La radiolisi dell'acqua è un fenomeno molto importante ed è indotto dalla radiazione del combustibile esausto, l'irraggiamento dell'acqua segue un meccanismo di reazione ben definito per cui è possibile quantificare le concentrazioni di specie radicaliche prodotte nell'acqua nelle condizioni a cui i contenitori di rame sono sottoposti.

Da precedenti studi è stato dimostrato che la simulazione con programmi di calcolo (MAKSIMA - chemist) del processo di corrosione della superficie di rame in contatto con le specie radicaliche disciolte in acqua è un fenomeno sottostimato. Da questi risultati scaturisce la necessità di testare il materiale interessato in condizioni simili a quelle sviluppate nel deposito per comprendere quali reazioni, finora sconosciute, avvengano sulla superficie e aggravino i fenomeni ossidativi.

La simulazione delle condizioni a cui il contenitore di rame verrebbe sottoposto nella realtà è un'operazione molto complessa, in scala sperimentale sono state apportate delle semplificazioni che non mettono in discussione la validità dei risultati.

Lo scopo dell'analisi sperimentale svolta è la valutazione e l'identificazione dei processi di corrosione che avvengono sulla superficie in rame utilizzata nei contenitori di combustibile esausto in KBS – 3 in presenza di acqua in condizioni anaerobiche. Lo svolgimento della sessione sperimentale utilizza principalmente due tipologie di prove:

- campioni sottoposti a irradiazione tramite sorgente γ in soluzione acquosa anossica

- campioni inseriti in soluzioni deaerate a diversa concentrazioni di perossido di idrogeno

Lo studio degli effetti prodotti dalla irradiazione sulle superfici interessate è comparato a uno studio sperimentale che valuta gli effetti della presenza in soluzione del perossido di idrogeno, questa specie è considerata il prodotto ossidante più importante della radiolisi dell'acqua.

La valutazione del processo di corrosione superficiale viene conseguita in modo differente a seconda dell'esperimento considerato e dei materiali utilizzati.

I materiali utilizzati per l'analisi della corrosione indotta da radiazione sulla superficie in rame del canister sono:

- provini cubici di rame di dimensione 1 cm^3 direttamente tagliati da un pezzo di parete del canister progettato per KBS – 3
- campioni di polvere di rame
- campioni di polvere di ossido di rame (I), detto cuprite
- campioni di polvere di ossido di rame(II), detto tenorite

Le analisi svolte sui campioni cubici di rame metallico hanno prodotto risultati complessi dal punto di vista cinetico, ma hanno evidenziato il peculiare ruolo del perossido di idrogeno nel processo di corrosione del rame in condizioni anaerobiche. Pur avendo ottenuto evidenti risultati del fenomeno, la cinetica di reazione è risultata complessa da definire. Per poter semplificare il sistema e comprendere al meglio le reazioni che avvengono sulla superficie di rame man mano che lo strato di ossido viene creato dai processi corrosivi, una sessione sperimentale condotta con polveri di rame e ossidi di rame è stata avviata.

Dalle analisi degli esperimenti condotti con campioni esposti a varie soluzioni di perossido di idrogeno è stato possibile valutare la cinetica di reazione di consumo di perossido di idrogeno in superficie e formazione di radicale ossidrile. Per poter quantificare le concentrazioni di queste due specie ossidanti sono stati utilizzati due metodi spettrofotometrici, il Metodo Ghormley per la quantificazione del perossido di idrogeno e il Metodo Modificato di Hantzsch per il radicale ossidrile.

La valutazione del processo ossidativo dei materiali sottoposti ai differenti esperimenti è stata condotta principalmente con sue strumentazioni:

- ICP (spettrometria di massa a plasma accoppiato induttivamente) per la determinazione di rame disciolto in soluzione
- SEM (microscopio elettronico a scansione) per la caratterizzazione delle superfici esposte a irradiazione e/o a soluzioni contenenti perossido di idrogeno

La valutazione della quantità di rame rilasciata in soluzione grazie all'analisi ICP permette la comparazione degli effetti ossidativi di alcuni materiali sottoposti a condizioni differenti.

Grazie alle analisi delle superfici condotte sui provini cubici di rame è stato possibile individuare gli effetti sulla superficie della presenza di perossido di idrogeno nel sistema e le differenze riscontrate con l'esposizione a radiazioni .

La sessione sperimentale effettuata sui provini di rame provenienti dal canister ha evidenziato una certa peculiarità di comportamento di alcuni provini. Per poter valutare le cause di certi comportamenti non riscontrabili in ciascun campione è necessario lo sviluppo di nuovi studi.

Fino ad ora i risultati ottenuti in questo lavoro sperimentale dimostrano che il rame in presenza di acqua idrolizzata in condizioni anaerobiche presenta predisposizione alla corrosione. Il potere ossidativo sul rame è stato principalmente attribuito alla presenza di perossido di idrogeno nel sistema, in esperimenti in cui il campione è sottoposto a soluzione di perossido di idrogeno e contemporaneamente a irradiazione è stato registrato un incremento significativo della corrosione superficiale. Lo studio condotto sui provini di polvere di rame e ossidi di rame ha consentito lo sviluppo di alcuni metodi d'analisi utilizzati nella sessione sperimentale dei campioni di canister ed ha consentito la determinazione delle reazioni che avvengono tra perossido di idrogeno e le singole superfici ossidate.

La analisi della cinetica di formazione del radicale ossidrile in esperimenti effettuati con le polveri ha consentito lo sviluppo di tecniche peculiari per lo studio cinetico dei campioni costituiti da rame metallico.

La valutazione diretta degli effetti prodotti dal radicale ossidrile nel sistema non è stata ancora definita in maniera completa perciò altri studi sono necessari al fine di poter avere un quadro completo delle reazioni che avvengono nel sistema considerato.

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Abstract

The long term safety of facilities that preserve the radioactive waste from the surrounding environment is one of the main concerns for countries that use nuclear power plant as main source of electrical energy. In Sweden the most developed concept of long term disposal of spent nuclear fuel is the KBS − 3 project, designed by SKB (the Swedish Nuclear Fuel and Waste Management Company). The project consists in a geological disposal site where the spent nuclear fuel will be placed in an iron cast insert sealed in a copper canister surrounded by bentonite clay and placed in the bedrock in tunnels 500 meters under the sea.

Some studies underline the importance of radiation induced corrosion of copper, but very few data are reported in literature.

The experimental analysis carried out in this work has the purpose to investigate the reactions involved in the radiation induced corrosion of copper in an anaerobic environment.

The process of the radiation induced surface corrosion is mainly due to the presence of products of water radiolysis: hydrogen peroxide and the hydroxyl radical are considered the most important ones. In previous studies, numerical simulations demonstrated that the aqueous radiation chemistry cannot be considered the only process driving copper corrosion.

In this work the investigation of the unknown reactions involved in radiation induced copper corrosion is carried out through experiments performed with samples of different materials exposed to gamma irradiation or to an aqueous anoxic environment filled with a certain amount of hydrogen peroxide.

The materials that have been investigated are: copper samples cut from the canister wall designed for KBS − 3, copper powder , copper oxides (cuprite and tenorite) powder.

The features of the corrosive processes on the surface of copper cube samples were examined qualitatively using the SEM (scanning electron microscope) technique, the results show that the combination of irradiation in an environment filled with hydrogen peroxide increase the dissolution of copper releases in solution.

The concentration of copper in solution after each experiment was measured with the ICP-AES (inductively coupled plasma atomic emission spectroscopy) spectrometer.

The methods used for the detection of hydrogen peroxide and hydroxyl radical dissolved in solution are the Ghormley and Modified Hantzsch spectrophotometric methods.

The crucial role of hydrogen peroxide in an aqueous anoxic environment is underlined in hydrogen peroxide experiments, the kinetics of consumption evaluated in these experiments show that this oxidant species is decomposed by catalytic decomposition on the oxide surface. This reaction produces hydroxyl radicals that are responsible of other corrosion processes on the surface. The role of this radical in the radiation induced corrosion of copper is not yet well understood, further investigations are required.

Chapter 1

KBS – 3 concept: an idea for a final repository for spent nuclear fuel

The handling of the nuclear radioactive waste in general is one of the main issues related to nuclear power. In this new century the challenge of finding a solution to this problem is more important than ever and several options have been taken in account. One of the most developed concepts for the final disposal of spent nuclear fuel is the Swedish KBS-3 concept. A brief description of the several options analysed by many countries for the disposal of spent nuclear fuel is presented in the next section, then a detailed description of the Swedish project is exposed.

1.1 Disposal of spent nuclear fuel: existing projects and future works

Radioactive materials are created not only during the production of energy in nuclear power plants but even in industrial and research activities for medical, environmental and agricultural applications. A waste management strategy that considers the whole sequence of waste handling from production until safe disposal has to be developed.

The purpose of a well developed radioactive waste management is to handle the waste in such a way that human health and environmental safety are ensured from the beginning and in the future. Waste management involves a chain of operations that can be listed into: handling, pretreatment, storage, transportation and finally the disposal of the conditioned waste. It also has to include the release and discharge of decontaminated materials.

The storage and the management of radioactive waste is completely different for low and intermediate level radioactive waste and high level waste. Another classification within the low and intermediate waste considers short lived and long lived waste, the former can be disposed even near the surface, the latter has to be sealed in geological disposal facilities.

The category of interest for this work is the disposal of spent nuclear fuel that is treated in the same manner of high level radioactive waste.

The spent nuclear fuel is uranium dioxide fuel that has been used and irradiated in a nuclear reactor and it is no more as efficient in splitting its atoms and producing heat to make electricity[1].

The reactor fuel is a solid and consists of a long metal tube filled with small fuel pellets. The radioactive elements in the spent nuclear fuel have mostly long half-lives (plutonium-239 and plutonium-240 present respectively 24000 and 6800 years of half-life).

Because of this the spent fuel has to be stored in a safe and controlled repository for thousands of years.

There are several options of disposal of spent nuclear fuel.

The first step of the disposal of the fuel is a temporary storage, a period that is roughly 50 – 100 years in which the decay of heat generation and the radioactivity decrease significantly. Only after this treatment the final storage is possible. This first disposal can be made in either a wet or dry environment, and can be placed close to the nuclear power plant or in another site. In the wet storage, the spent fuel elements are placed in designed water-pools, the shielding of the fuel is achieved with at least a depth of 20 feet of water. This solution was first designed for a short period of storage but due to delays in designing of storage facilities in most cases these pools were redesigned to allow a higher number of nuclear fuel rods for longer time. Anyway, the design of this disposal is limited by the size of the spent fuel pool. It is necessary to maintain a safety distance between all the rods. As it is not possible to enlarge the pools in order to store all the spent fuel on a permanent basis, this storage can only be used as a temporary solution.

The second option is dry storage in which the fuel is sealed in containers called casks. These vessels can be made by metal or concrete, the fuel is protected by an atmosphere of inert gas and the cans can be placed horizontally or vertically. These storage facilities vary from bunkers made in concrete capable to withstand plane crashes to open air ones.

The last step of a permanent storage of the nuclear spent fuel is a concept that has been debated for many years in various countries in the world but so far there are no operative storage facilities for permanent storage of high level waste.

Some concepts have been designed and are planned to become operational within roughly 15 years in Europe: Belgium, Finland, Netherlands, Sweden and France [1]. A strong debate is going on in the USA for the project of a permanent disposal facility to be placed in Nevada in the Yucca Mountain. The controversy does not regard anymore any safety or environmental issue of the proposed site but is more of a controversy between the state and local authorities.

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[1] "Radioactive waste : production, storage, disposal" US Nuclear Regulatory Commission

1.1.1 Permanent disposal approaches

In every country having nuclear power, the choice regarding the kind of for permanent repository for spent nuclear fuel has been debated for long time.

All the options taken into account were discussed in detail in the Department of Energy's final Environmental Impact Statement on the Management of Commercially Generated Radioactive Waste [2]. The disposal options considered are : disposal in mined geological formation, in multinational repository, in underground nuclear test cavities, in seabed, in deep boreholes, in permafrost and finally into the space.

A brief description of all the options is given here below.[3]

Mined geological formation

The option to seal the high-level radioactive waste into a mined geological formation, that can be a salt, granite, tuff, basalt or clay environment was considered the most immediate solution for this problem for over fifty years. In many countries the disposal few hundred meters below the surface was considered. Depending on the environment present in the territory many geologic environments were investigated. Some proposed deep geological repositories are in salt domes in Germany (Gorleben), into argillite in the Bure underground research laboratory in eastern France, in granite and sedimentary rocks in Japan and Canada, in granite bedrocks in Sweden and Finland, or in clay environment in Switzerland (Mont Terri) and Belgium (Mol).

In the U.S. several options of geologic repositories were investigated : three sites were in salt domes, other four were in bedded salt, one in basalt and only another one was considered in a volcanic tuff environment : the Yucca Mountain, in Nevada. This site is the only one which has an unsaturated zone with reducing chemical conditions, these particular characteristics make this site the only candidate for a permanent repository .

The reducing conditions are advantageous for a site where long term waste isolation has to be maintained, since many long-lived radionuclides present a much lower solubility and mobility under these conditions compared to oxidizing ones. Moreover, it has been demonstrated that the UO_2 which is the chemical form of commercial spent fuel is stable in reducing environments so that the releases of fission products are assumed to be limited.

Multinational repository

Considerable attention has been given to the plan of a multinational repository including the usage of unoccupied islands. One of the motivations that support this concept is that most of the smaller countries which have nuclear power plants do not have a suitable site for a repository. Furthermore the cost required to build a national facility can be very unattractive compared to a multinationally controlled repository. Support for this option is mainly given

by the IAEA, the International Atomic Energy Agency, which would be involved as safeguard institution. Although there are many positive aspects, there are of course also many negative and ethical considerations which did not advance the development of an international repository as a possible solution.

<u>In situ melting</u>

The idea of this disposal method is to put liquid waste from reprocessing into an underground cavity, which can be an underground nuclear weapons testing. The sealing would be performed by the heat of the waste that would melt the rock producing a glassy cover which ensure the shielding. The project would also consider a reprocessing plant closely located to the underground nuclear facility.

<u>In seabed</u>

The disposal considers emplacement of waste canisters under a thick layers of mud and clays of the ocean floor. This concept did not find any popularity.

<u>In deep boreholes</u>

The concept of deep boreholes considers the drilling of a hole of a certain depth in which the bottom is then filled with vitrified high-level waste or spent fuel. The sealing is performed with some backfill which can be cement or other materials, depending on the waste considered. This concept was introduced by SKB (the Swedish Nuclear Fuel and Waste Management Company) in 1989 and further modifications were made on this. The Swedish repository project considers waste canisters made by copper enclosed by low permeability clay, the reducing conditions of this environment ensure an extreme long lasting corrosion resistance of copper.

The deep borehole concept can be a competitive solution compared with the mined repository in terms of costs and safety measures.

<u>In the deep space</u>

The launch of the waste in the orbit has been also taken into account, not all the high-level radioactive waste is considered to be treated in this way because of the very high cost to place objects in the space. The waste that would be disposed in this way is only a small part of the total, that is the very long lived waste. This option is mainly due to the fact that reduction of the weight of the considered waste is necessary. Even after this consideration the cost would be really high. Furthermore the risks and the capabilities of todays technologies to separate the nuclear waste and to move the material into space have to be improved.

The last hypothesis considered in order to find a solution to the problem of nuclear waste disposal is the method of spent fuel reprocessing. This process is not really a storage method

but it allows a significant volume reduction of disposable waste to dispose due to the recover of uranium and plutonium. The fact that so far the usage of new uranium fuel is cheaper and easier than the use of reprocessed mixed oxide fuel make the consideration of this option more difficult. Another alternative could be the usage of reprocessed spent fuel in fast breeder reactors. These can further produce more fuel than they deplete.

The fact that the amount of long lived radionuclides is really small compared to the entire volume of the nuclear waste to store makes the economic evaluation of whether to reprocess or not a very complex issue. Only if the use of nuclear power will increase in the next decades the spent nuclear fuel may be regarded as a resource rather than a waste and reprocessing would become increasingly important.

1.2 The SKB system for managing radioactive waste

The Swedish Nuclear Fuel and Waste Management Company, SKB, has developed a complete system which handles the radioactive waste from the point where the waste is produced in nuclear power plants until the final storage.

Waste that needs to be transported is placed on the ship M/S Sigyn. The spent nuclear fuel is shipped to CLAB (the central interim storage facility for spent nuclear fuel). All the short lived and low-intermediate level waste is stored in SFR: a final storage of low level waste.

In Sweden the method used for the disposal of the spent nuclear fuel is encapsulation in canisters and storage in a deep geological repository in crystalline bedrock. The final repository for short-lived radioactive waste, SFR, was opened in 1988 and was placed close to the Forsmark Nuclear Power Plant where three boiling water reactors are in operation. The repository contains low and intermediate level operational waste such as clothes, replaced parts from nuclear power plants, filters and ion exchangers. In addiction radioactive materials from health care, industry and research are also placed in SFR.

The existing SFR repository has a capacity of 63000 m^3, the waste is stored in rock vaults at a depth of roughly 50 metres under the ground inside metal or concrete containers. The storage is kept under severe surveillance, all the materials stored will lose their radioactivity after approximately 500 years. SKB now wants to extend this repository by building a new section with the same characteristics, placed beside the existing repository. The extension is needed for the dismantling of nuclear power plants in the future. In this case, the waste from nuclear facilities in Sweden would be stored here. The volume of decommissioning waste is expected to be twice as much as the operational waste. It includes reactor components, scrap metal and concrete from building materials. The decommissioning waste would be stored in the same way as the operational waste, so the extension will be planned on the basis of the SFR concept. Thanks to the enlargement of this repository, expected to be operational by 2023, SFR will have space for the disposal of 200000 m^3 of waste.

The new area for the decommissioning waste will consist of six new rock vaults that reach deeper depth, approximately 120 metres below the seabed, where suitable bedrock is present. The tunnel which will connect the new part of the repository will be built large enough to transfer reactor vessels in it. [4]

An illustration of the layout of the SFR project can be seen in Figure 1.

The low level waste does not need any radiation shielding and can be stored in ordinary steel containers, while the intermediate level waste is poured into concrete and steel containers. This includes the operational waste, some components of the decommissioning waste as reactor rods need to be isolated for thousands of years instead of 500 years. [5]

The smallest part of the total waste to handle is the most hazardous one: the spent nuclear fuel. It has to be stored for at least 100 000 years and has to be radiation shielded and cooled during the whole process of handling, transportation and storage. For this reason the spent nuclear fuel disposal requires a special concept, the so called KBS-3.
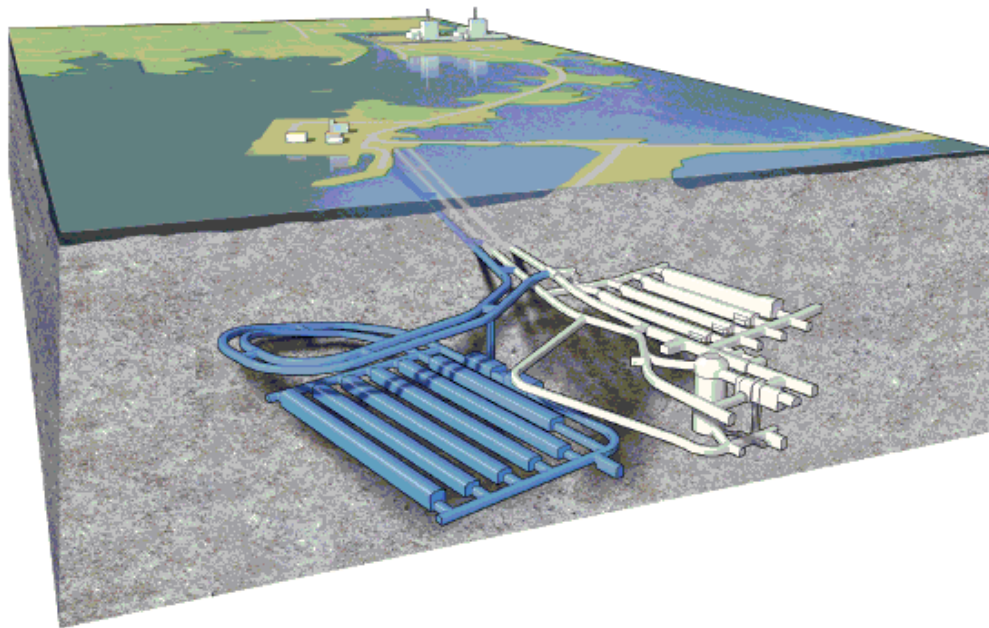
Figure 1. The existing repository, SFR, in grey on the right. The future planned extension consists of the blue tunnels on the left.

1.3 Description of KBS-3: final repository of spent nuclear fuel

The solution proposed by SKB is to handle the spent nuclear fuel in a geological final repository that would be situated in Östhammar.

The selection of the site was made after thorough analysis of many different places, the site investigation shows that a very solid bed rock is present in Östhammar. At the selected site the bed rock presents few fractures and a small percentage of water, conditions that allow a

much easier construction of the facility. The presence of water is hazardous in terms of corrosion of the components involved in the repository.

The aim of the final repository is first to isolate the spent fuel from the presence of humans and protect the environment for at least 100000 years. Furthermore in case of canister break, the repository itself should retard any possible release of radionuclides. The design of the repository must fulfil the authorities' requirement regarding the maximum average dose for human beings of about one per cent of the natural background radiation.

The design developed by SKB for the final repository is based on three barriers which protect the environment from the radionuclides of spent nuclear fuel.

The three barriers involved are, from the outer until the inner one, the bed rock – the bentonite buffer – and the canister that seal the spent nuclear fuel from the environment.

The fuel elements are first cooled for a period of at least 30 years and then are placed in the cast iron canisters with the copper sleeve.

The technology that is going to be used is still being tested in a full scale facility in a real environment, this is the Äspö Hard Rock Laboratory and the Canister Laboratory in Oskarshamn. Of course the very long time perspective of 100000 years of stability and safety in the repository is a challenging request. However it is well known that the Swedish crystalline bed rock was stable for billions of years.

All the problems that could occur during the lifetime of the repository are taken into account: even the capability of the materials involved to withstand a possible future ice age era is studied.

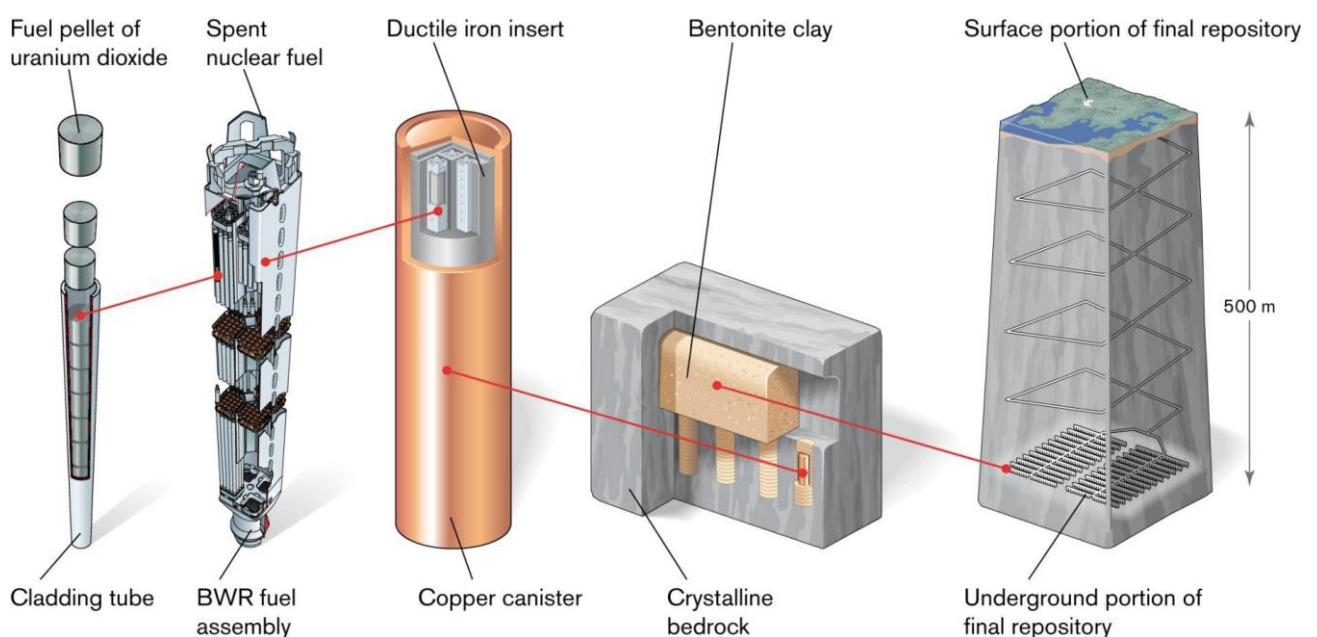The pictures below show the concept of the spent fuel repository.

Figure 2. The final repository barriers: they ensure a shielding of radioactive substances

A brief description of the properties of the three barriers follows.

The bedrock

The choice of bedrock as geologic disposal is based on the capability of this environment to isolate the repository from the biosphere and the surface processes. The secondary aim, but not less important, is the function of delaying the releases of radionuclides in case of damage of the first two barriers. The delay is attributed to the rock properties. The solid rock has few fractures and the great depth of the deposit allow a perfect isolation of the spent nuclear fuel. The most common radionuclides in the fuel are cations. As most mineral surfaces are negatively charged, the radionuclides would be adsorbed by the rock and the transport towards the surface would be retarded.

Another important aspect that was taken into account is the presence of groundwater in the rock, it is important for the canisters and the buffer to have a low renewal of water.

After the filling of the repository the tunnels made for the transportation and the rock caverns will be sealed, the backfilling will keep the conditions of the repository stable.

The bentonite buffer

The canisters are embedded in the bentonite clay which acts as a buffer and protects the copper coating from corrosion and rock movements. The clay has to be mechanically and chemically stable, it has to absorb the movements that occur in the rock and buffer the chemical changes of the groundwater. The diffusion of corrosion products, radionuclides, colloids and particles in general is retarded by the clay. The bentonite clay used consists of 70 − 80 % montmorillonite, when in contact with water it swells and fills the cavities between the canister and the bedrock. The swelling pressure is up to 100 bars, this allows a total isolation from corrosion processes or the release of radionuclides up to the surface, all the transports to and from the canisters will be driven by slow diffusion processes.

The copper canisters

The copper canisters are placed in the crystalline basement rock at a depth of 500 metres, embedded in the bentonite clay.

The copper itself contains the spent fuel. It has the main role of first shielding so it has to be gas and water tight. This first barrier should withstand any corrosion process for a period of at least 100 000 years in order to protect the spent nuclear fuel until it reaches a natural level of radioactivity. The canisters also have to be mechanically strong to withstand accidental shocks during the disposal operations. The design of the canisters must give them sufficient protection for radiation and appropriate thermal conductivity. They must also be able to resist deformation forces, internal pressure, swelling pressure. They are made to withstand possible future ice era and earthquakes.

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The canisters will be nearly five meters long and approximately more than one meter in diameter, after the filling with the fuel assemblies their weight is about 25 tonnes.

In order to preserve the purity of the copper until the final disposal in the repository during the deposition of the canisters it will be planned a surface contamination control process between them and the equipment necessary for the handling.

The canisters will be sealed with a welded copper cap so no radioactive substances will escape, the copper cover of the cast-iron insert which contains 12 fuel assemblies is five centimetres thick (see Figure 3). It is made by extra pure copper with Cu 99,99% minimum with some impurities of silver, iron, phosphorus (respectively 25 – 10 – 30/70 ppm maximum). The cast iron insert give strength to the canister, the copper was chosen due to its high resistance to corrosion.

The copper canister needs to be stable to gamma and neutron radiation that comes from the disintegrations of the fuel, the radiation is converted mostly into thermal energy. The dissipation of the heat is mainly made through the canister. The heat generation in the canister due to radiation may induce changes in the mechanical properties. The designs of the canisters and the iron insert are based on thermal models based on the heat transport calculations that consider the iron insert, the copper canister and the air gap between them. All the calculations are based on pessimistic data for copper surface temperature, copper emissivity and the size of copper and iron gap.

Mechanical interactions between the buffer and the canisters were studied together with studies on pressure changes due to the canister corrosion products. [6]

Figure 3. The ductile cast-iron insert in which are placed the twelve fuel assemblies.

One of the main problem due to corrosion of copper is the galvanic processes which may occur on the surface if water comes in contact with the cast iron insert. The cast iron corrosion rate evaluated was very high (up to 100 µm a year) [6], but in case of any intrusion of water, the water itself is considered oxygen-free and so the corrosion rates are expected to be negligible.

The process of copper corrosion due to oxygen trapped in the air space in the buffer or available in the groundwater was analysed. Furthermore corrosion processes due to nitric acid were taken into account, they are formed by gamma radiolysis in contact with nitrogen of the filling. The corrosive action of various oxidants due to radiolysis of water and sulphides transported from the groundwater via buffer were also investigated. [6]

It was demonstrated that these phenomena do not affect the mechanical stability of the canister, furthermore it was considered that copper is thermodynamically immune to corrosion in pure water in anoxic conditions.

1.4 Introduction to the work

The publications by some researchers, Hultqvist and Szakalos, about the possibility of corrosion of copper metal even in pure water without any complexing ions such as sulphides and chlorides give some doubts regarding the time perspective of stability of the copper canisters for 100 000 years.

These researchers claim that the copper canisters may collapse in 1000 years. [7]

Another very recent study demonstrates that metallic copper will corrode faster than what was expected after being exposed to ionizing radiation.

The purpose of this work is to evaluate the processes that occur at the surface of metallic copper in a system of anoxic water in which some products of water radiolysis are dissolved.

The radiation induced corrosion of copper in an anaerobic environment has been studied experimentally.

The next chapters present the experimental analysis carried out on copper samples in order to better evaluate the behaviour of the metallic copper surface, used as main barrier in KBS – 3 project, exposed to irradiation in contact with anoxic water.

In Chapter 2 an analysis performed in previous papers on copper cube samples cut from a KBS – 3 canister wall is shown. The samples were exposed to gamma irradiation and the effect of this irradiation were evaluated with SEM, IRAS, AFM and ICP.

From Chapter 3 the experimental results performed for this work are shown. The experiments here performed consists in iron, copper and stainless steel exposed to gamma irradiation and hydrogen peroxide experiments.

In Chapter 4 and 5 the results from samples of copper powder and copper oxides powder exposed to hydrogen peroxide experiments are presented. The analysis on powder samples

allows the evaluation of the kinetics of the decomposition of hydrogen peroxide on the surface and the production of hydroxyl radicals in the system.

In Chapter 6 the analysis on copper cube samples exposed to hydrogen peroxide experiments and gamma irradiation experiments is presented. The corrosion processes on the surface are evaluated with the ICP analysis and the SEM analysis.

In Chapter 7 all the results achieved in copper powder, copper oxides powder and copper cubic samples are compared and described in details.

The analysis of the kinetics of decomposition of hydrogen peroxide on powder samples was fundamental in the explanation of the kinetics evaluated in copper cube samples. The corrosive features of the cubic samples were compared with the experiments described in Chapter 2. It is here demonstrated the crucial role of hydrogen peroxide as main cause of irradiation induced copper corrosion.

Chapter 2

Materials involved in the KBS-3 concept: crucial role of copper

In the KBS-3 concept, the copper was chosen as main barrier against radioactive releases from the spent nuclear fuel due to its corrosion resistance. The few existing previous studies reveal that the corrosion process between the copper surface and products of water radiolysis is not yet well understood. This chapter presents the results gained in previous studies in which the consequences of corrosion due to gamma irradiation were investigated.

2.1 Radiation induced corrosion of copper

The decision to use pure copper canisters as a first barrier in the disposal of high level nuclear waste in Sweden has been debated in the last years.

The main problem that has been taken into account is whether or not the copper metal in pure water under anaerobic conditions is able to withstand any corrosion process.

Copper metal reaches a thermodynamically-immune state under conditions of anoxic pure water, but the environment in which the repository is going to be built has characteristics that are far from being pure and stable. Species that are able to activate the corrosion of copper are present in the system considered, one of these is the sulphide ion. The corrosion of the metallic canister is related to the rate of transport of this ion towards the copper surface. SKB has estimated the rate of corrosion in 10 nm/year [8], this results into a corroded depth of roughly 1 mm over a 100000 year storage period which is well lower than the 5 cm of corrosion allowance for the current canister design. [9]

There are several studies which investigate the role of different species present in the groundwater that can react with copper causing the corrosion enhancement. The main products which can react with the canisters and thereby decrease its life time are sulphur species, dissolved gas (hydrogen and carbon dioxide), chloride ion and pyrite. [9]

Another issue that had received less attention is the impact of radiolysis of water on the corrosion of copper. Radiolysis of water produces a number of reactive species such as O_2, H_2O_2, H_2, OH, O_2^-, H, OH, H^+ and OH^-,. Theissue is to ascertain if this phenomenon is a crucial factor in the corrosion of copper in the KBS-3 granitic rock repository.

2.1.1 Impact of water radiolysis on copper corrosion

Water radiolysis is the decomposition of water molecules due to ionizing radiation [10]. The consequence of this phenomenon is the production of many species such as the solvated electron (e^-_{aq}), the hydroxyl radical ($\cdot OH$), hydrogen gas (H_2) and hydrogen peroxide (H_2O_2). The water radiolysis can occur in several situations ranging from radiotherapy to nuclear reactor environment. In this work the main discussion is the consequence of water radiolysis on the corrosion of copper canister occurring in the future storage of spent nuclear fuel.

The two most important species to take into account among the water radiolysis products are the OH - radical and hydrogen peroxide due to their oxidizing nature. These two species are able to cause corrosion of materials used in nuclear reactors and in spent nuclear fuel storages. In order to avoid corrosion induced accidents it is of great importance to understand their behavior in such environments.

It is well known that in anoxic aqueous environment, radiation damages and corrosion processes mainly depend on the reactions that occur at the metallic interface with products of water radiolysis. [11]

Despite the critical role of these interactions, the mechanism of these reactions at the molecular scale are not well knwon.
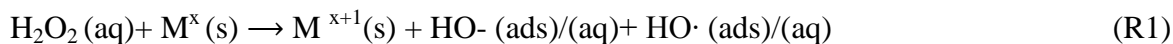
An example of anoxic aqueous system, in which metallic surfaces are exposed to radiation and radiolysis products, is indeed the SKB final repository for spent nuclear fuel. The spent nuclear fuel is sealed at a depth of 500 meters into bedrocks and protected with three barriers which the first one is the encapsulation in copper canisters with ductile iron inserts, the second one is the bentonite-clay buffer that is finally placed into the crystalline basement rock. The rock is the third barrier because it serves to isolate the repository from accidents that happen at ground level and it will retard possible radioactive releases. Since the bedrock is not completely impermeable, the copper canisters are protected by the bentonite clay that acts as a buffer. Copper has been chosen for its corrosion resistance, but still few studies were performed under conditions of radiation induced corrosion of copper in anoxic conditions.

The gamma radiation originating from the spent nuclear fuel is able to penetrate the copper canisters, if water is in contact with them it undergoes radiolysis and the products formed (H_2O_2 and $OH\cdot$) might corrode the metallic surface.
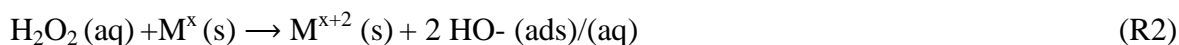
In principle, hydrogen peroxide can react with metal oxide surfaces via three different pathways (1) : one electron oxidation (R1), two electron oxidation (R2), and catalytic decomposition (reactions (R3)-(R5)). [12]

In the mechanism presented below (1): M represents a metal atom in the metal oxide and x and y its oxidation states. [12]
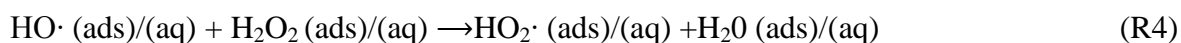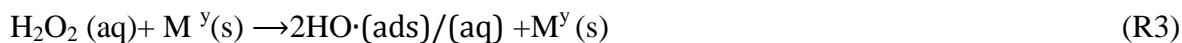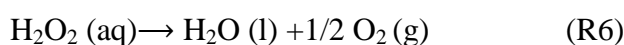
One- electron oxidation:

$$H_2O_2\,(aq) + M^x\,(s) \longrightarrow M^{x+1}(s) + HO\text{-}\,(ads)/(aq) + HO\cdot\,(ads)/(aq) \qquad (R1)$$

Two electron oxidation :

$$H_2O_2\,(aq) + M^x\,(s) \longrightarrow M^{x+2}\,(s) + 2\,HO\text{-}\,(ads)/(aq) \qquad (R2)$$

Catalytic decomposition:

$$H_2O_2\,(aq) + M^y(s) \longrightarrow 2HO\cdot(ads)/(aq) + M^y\,(s) \qquad (R3)$$

$$HO\cdot\,(ads)/(aq) + H_2O_2\,(ads)/(aq) \longrightarrow HO_2\cdot\,(ads)/(aq) + H_2O\,(ads)/(aq) \qquad (R4)$$

$$2HO_2\cdot\,(ads)/(aq) \longrightarrow H_2O_2\,(aq) + O_2\,(g) \qquad (R5)$$

From which the overall known stoichiometry is:

$$H_2O_2\,(aq) \longrightarrow H_2O\,(l) + 1/2\,O_2\,(g) \qquad (R6)$$

It is still not clear which reactions occur and in which manner the H_2O_2 competes with the presence of the others radiolysis products in an anoxic water system. Despite the presence of much more powerful oxidants, as the HO·, the H_2O_2 is a molecular species and therefore has longer lifetime thus the contribution of hydrogen peroxide to the oxidative power of the water radiolysis products is greater than that one of hydroxyl radical.

The aim of this study is to investigate how hydrogen peroxide interacts with some selected metal, especially copper, and its metal oxide surfaces as cuprite and tenorite.

It has been already demonstrated that the two most oxidizing species from radiolysis of water, the hydroxyl radical and the hydrogen peroxide, present a higher standard reduction potential than copper (see Table 2.1). This means that these species are capable to corrode the copper surface of the canisters from a thermodynamic point of view.

Table 2.1. *The standard reduction potential versus SHE (Standard Hydrogen Electrode) for hydrogen peroxide, the hydroxyl radical and copper*

Species	E° vs SHE [V]	Reference
$H_2O_2/2H_2O$	1.77	[13]
HO_{aq}/H_2O	2.59	[14]
$Cu^+/Cu(s)$	0.52	[15]
$Cu^{2+}/Cu(s)$	0.341	[15]

The oxidants species taken into account are products of water radiolysis due to the ionizing radiation coming from the spent nuclear fuel which penetrates the copper canister and gets in contact with water. Despite the importance of this phenomenon, only few studies have been reported on this matter. The process that has to be investigated is the corrosion of copper induced by gamma radiation in an environment of anoxic pure water.

After the closure of the tunnels there is an amount of oxygen in the repository at the moment in which the groundwater enters, but only a small amount of oxygen is supposed to reach the canisters. The initial concentration of oxygen will be consumed by bacteria, reducing minerals present in the rock and the bentonite and finally by a minimum corrosion process of the copper canister.

The gamma radiation is mainly produced by the nuclide Cs-137 and its half-life has been evaluated in 30 years [16]. For this reason the corrosion induced by radiation has a crucial role in the initial phase of the storage of the canisters in the deep repository.

2.1.2 Copper canister samples: irradiation experiments

Studies carried out on the energy transferred by the gamma and neutron radiation due to the radioactive disintegration of the fuel through the copper shell show a limit in the dose rate received by the canister.

The maximum total radiation dose that is going to interact with the outer canister surface has been evaluated in 100 kGy (1 Gy = 1 J/kg) for the initial period of 100 years in the repository[16]. This total dose is converted into a dose rate of 0.114 Gy/h.

In order to investigate the corrosion process of copper due to irradiation, various experiments were carried out in previous works. The effect of gamma radiation was studied under anoxic conditions in pure water at room temperature. The radiation was performed using a MDS Nordion 1000 Elite Cs-137 gamma source [17]. The dose rates employed during the experiments depend on the position of the sample and on the level of shielding used. Values of dose rates were evaluated using a Fricke Dosimetry (see figure 3.2).

The samples mentioned above are a 1 cm^3 polished copper cube placed in a glass beaker filled by 10 ml of pure deaerated Millipore Milli-Q water (18.2 $M\Omega cm^{-1}$). The irradiations were performed at room temperature and the pH of approximately 6 of the solution was checked with a Merck pH-indicator paper.

The copper cubes samples were taken from a piece of copper canister wall donated by SKB and this piece had the same characteristics of the canisters which are supposed to be placed in the repository: 99.992% Cu, major impurities are Ag and P. Every copper cube has the size of $10\times10\times10$ mm^3, the polishing on them was carried out with a SiC abrasive paper of 800 grid. One face of the cube was further polished with a 3 µm polycrystalline diamond paste (Struers). The polishing process was performed with a 99.5% solution of ethanol, after this the cubes were put in a solution 95% of ethanol in an ultra-sonic bath for approximately 5 minutes. The cleaning process was completed using acetone and finally the drying process was carried out in a glovebox with a flow of N_2 gas (AGA Gas AB, purity of 99.996%). The cubes were placed inside the glass baker with the finely polished side up.

Each experiment was performed by using two different pieces of copper cubes simultaneously; a reference sample was also used and was treated at the same manner of the irradiated ones.

The dose rates and the total dose used in each experiment are shown in the Table 2.2.

The studies funded by SKB show that the copper canister surface is supposed to be irradiated by a dose rate of approximately 0.114 Gy/h for approximately the first 100 years, this irradiation is produced by a total dose estimated in 100 kGy. The choice made in the experiments was to represent a total dose that is similar to the one evaluated for the repository, that is 100 kGy, while the reproduction of the same level of dose rate is no possible because of the long period it would need.

In the next table are summarized the characteristics of each experiment performed.

Table 2.2 *Total doses and dose rates used in every irradiation experiment*

Experiment	Dose rate [Gy/h]	Irradiation time [h]	Total dose [kGy]
1) reference [18]	360	168	62
2) reference [18]	756	168	129
3) reference [16]	80	462	37
4) reference [16]	770	48	37
5) reference [16]	370	96	35.5
6) reference [16]	770	96	74
7) reference [16]	---	---	0.74 – 1.5

In order to characterize and quantify the corrosion process induced by radiation, several analysis were carried out. The aim of the study was to evaluate the dissolution of copper in the aqueous solution and to make a surface characterization of the copper cubes.

Several analytical instruments were used for the characterization of the surface:

IRAS : a Digilab FTS 40 Pro Infrared Reflection Absorption Spectrometer

SEM: a Jeol JSM-6490LV Scanning Electron Microscope

AFM: an Agilent 5500 Atomic Force Microscope

The quantification of the amount of dissolved copper in solution was performed using an inductively coupled plasma atomic emission spectroscopy (Thermo Scientific iCAP 6000 series ICP spectrometer).

The experiments were carried out at different total doses that are within the range that is relevant in the deep repository.

The results of surface characterization and trace elemental analysis are presented in the following paragraphs.

2.1.2.1 Surface Characterization

The experiments 1) and 2) show a relevant corrosion of metallic copper cubes due to irradiation. As it can be seen in the Figure 2.1 [18] the reference sample presents a homogeneous surface while at increasing of the total dose the corrosion effect increases. The surfaces of the two irradiated cubes present a dark orange layer with black/brownish spots on the margins. The cube on the right got the highest total dose of 129 kGy and presents a much more relevant presence of black marks on the surface compared to the cube in the middle that was exposed to a total dose of 62 kGy.

The analysis with IRAS shows that the corroded layer is mainly due to the species Cu_2O, namely cuprite, that is an oxide mineral composed by copper (I) oxide.
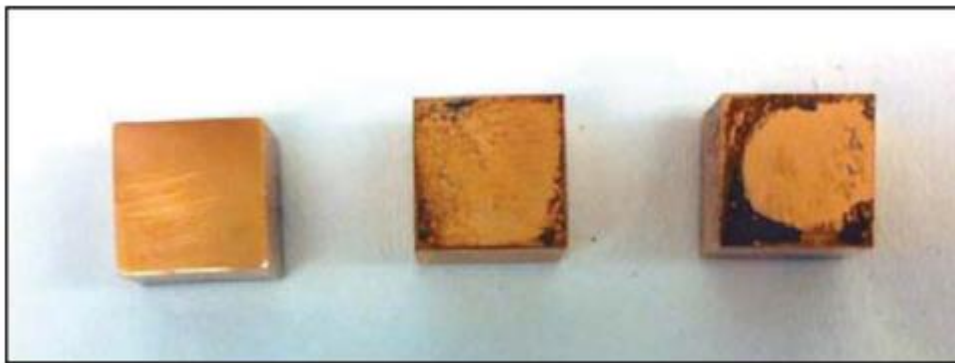

Figure 2.1 Photography of experimental set 1) and 2) of copper cubes. In order from the left side can be seen : reference sample – sample exposed to a total dose of 62 kGy - sample exposed to a total dose of 129 kGy

Thanks to the analysis on the surface by SEM was possible to see the morphology of the crystalline oxide layers. The irradiated samples show a particular characteristic on the surface: all over the surface are present circular shaped corrosion features of different size form and depth. Others smaller corrosion features shaped as holes are seen inside and outside the circular ones. All these features are shown in the Figure 2.2 [18].
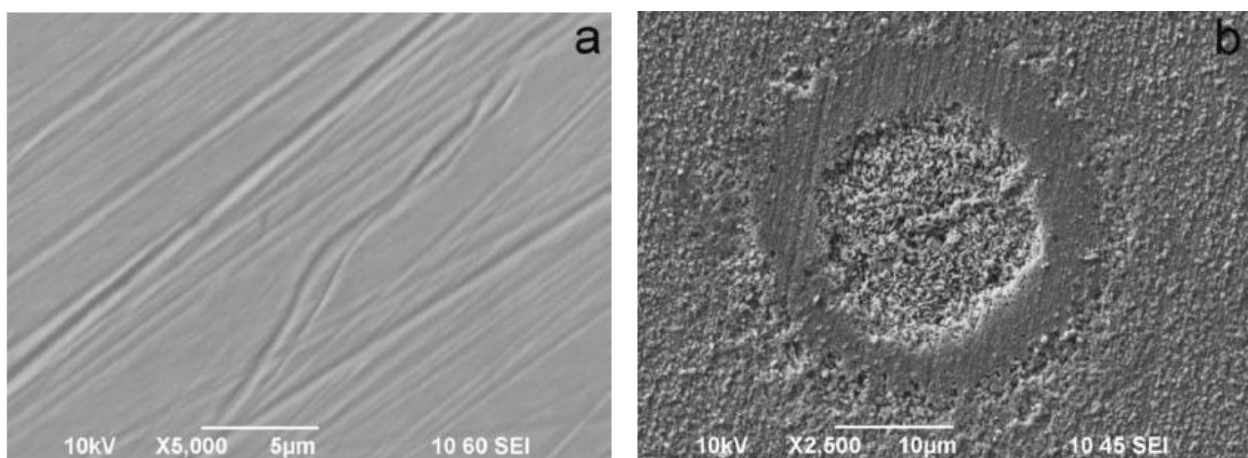

Figure 2.2 SEM images of different samples surfaces. The surface a) belongs to a reference non irradiated sample, the surface b) belongs to an irradiated sample.

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The surface of the reference sample is flat and presents only polishing markings, no corrosion features are shown. The irradiated sample surface has circular features, the ring is flat while in the center the surface is rough and excavated. The circular features vary between the different samples in shape: from smooth circular surface to a rough crater. Comparisons between analyses on the two samples irradiated with different doses show no relevant difference in size and shape. The analysis with AFM shows that the ring is flat and has a similar height as the outer surrounding surface. The central part on the contrary is approximately 800 nm deeper, this result can be seen in Figure 2.3 [18].
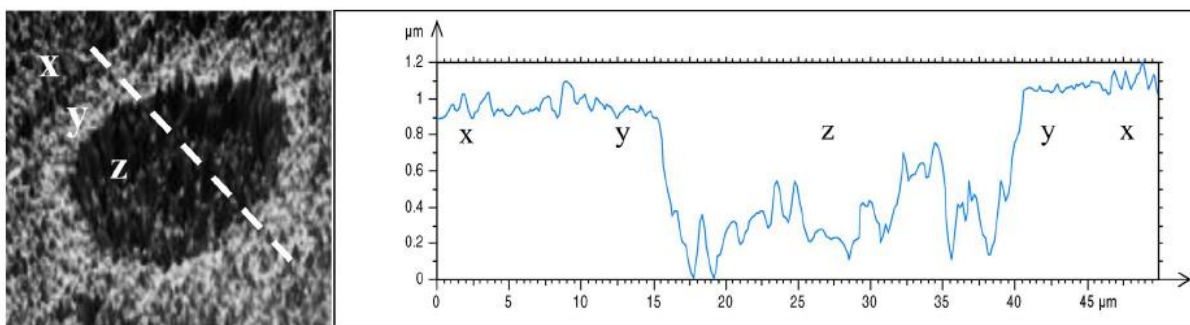

Figure 2.3 AFM topographic image of a circular corrosion feature. The central area z has a rough surface morphology and present an excavated area of 800nm depth than the surrounding area. The circular ring area y is smoother than the x outer surface.

The experiments 3), 4), 5), 6) show the same surface features on the irradiated samples. Cuprite was identified as the main corrosion product, together with a small amount of tenorite. Using the electrochemical method cathodic reduction it was possible to characterize the oxide layer due to irradiation as a really heterogeneous one. The oxide layer for all the samples was measured as a $50 - 100$ nm of thickness.

2.1.2.2 Dissolution of copper

The ICP analysis on anoxic water of the glass beaker of experiments 1) and 2) shows a significantly more relevant amount of copper dissolved at higher doses of irradiation. In the experiment 7) was even detected corrosion of the surface in samples where the surface characterization was not able to show it. At a total dose of 1.5 kGy there was a relevant amount of copper dissolved in water compared to the reference non irradiated sample, while for experiments at lower doses was not detected any difference between the irradiated and the non-irradiated sample. In experiments in the range of 0.74 -1.5 kGy the copper concentration for all the samples was approximately of 2 μM. This value is really close to the value of solubility of cuprite, so that even the reference samples present this amount dissolved.

Cuprite and tenorite solubility values in water at 25 °C and at pH = 5.5 has been evaluated in 3 and 30 μM respectively [19]. In experiments 3), 4), 5), 6) there is a significant difference between reference samples and irradiated ones considering the amount of dissolved copper.

At higher doses higher concentrations of dissolved copper are detected. Comparing samples exposed to the same total dose but with different dose rates it is not possible to see significant differences in term of copper release.

The relevant characteristic is that, in experiments at same total dose, samples irradiated with a lower dose rate for longer time present a higher amount of dissolved copper in water. A summary of the ICP data obtained in the various experiments is shown in Figure 2.4 [16].
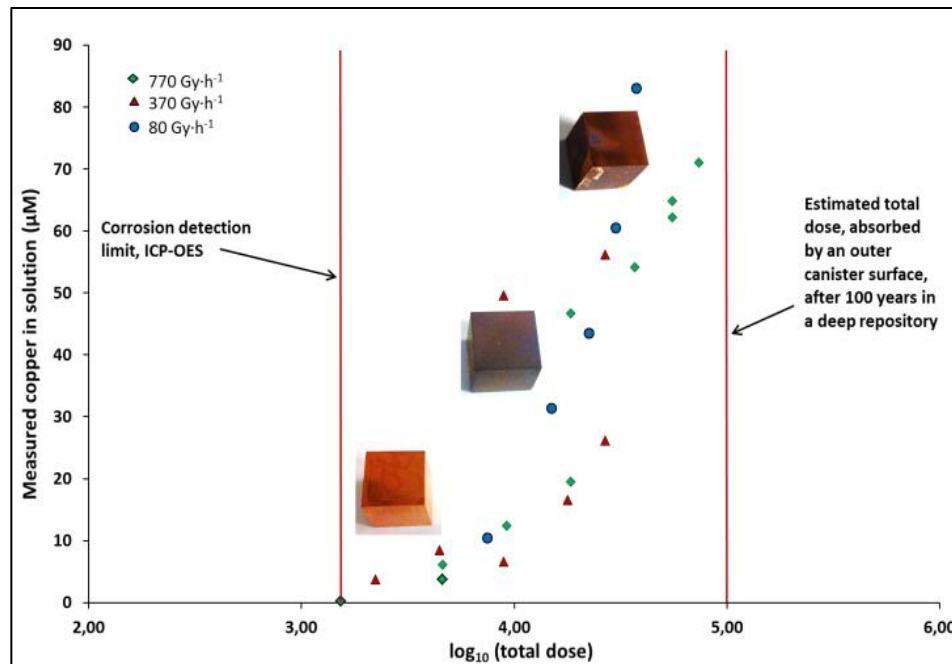

Figure 2.4 ICP results on experiments of irradiation in aqueous anoxic water. Dissolution of copper is presented in relation with the total dose and dose rates used. Picture of copper cubes irradiated at total doses of 1.5 – 37 – 74 kGy are also shown.

In order to predict the corrosion process of the copper canister surface driven by gamma irradiation, some studies were done using to the software MAKSIMA-chemist. This program was used in previous works in order to evaluate and simulate the dissolution of pure uranium dioxide powder in water under gamma irradiation [20]. In this case the simulation showed a good agreement between numerical and experimental results so that it is demonstrated that the dissolution of uranium dioxide is governed by the reactions occurring in water radiolysis process. The same principle is applicable here, in order to demonstrate that the observed phenomenon of radiation induced corrosion of copper is mainly driven by the radiolytic oxidants, a numerical simulation was performed. First the concentrations of radiolytic species were simulated, on the basis of the reactions involved in the known mechanism of radiolysis. In the case of heterogeneous system, in which the solid surface area to solution volume ratio is low enough, the surface reactions will not influence the concentrations of radiolysis species in the bulk. In the radiation induced corrosion of copper the solid surface area to volume of

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solution ratio is three times lower than the one of the uranium dioxide study, so the simulation is still valid.

The concentrations of radiolysis products are then used in order to evaluate the rate of oxidation due to surface reactions. From the rate of oxidants is then possible to evaluate the rate of oxidation at a given time thanks to equation (2). To calculate the total amount of oxidized copper is then necessary to integrate equation over time. [16]

$$Rate = \frac{dn_{Cu}}{dt} = A_{Cu} \sum_{ox=1}^{n} k_{ox} [Ox] \frac{n_{e^-}}{2} \qquad (2)$$

In the equation:

A_{Cu} : surface area of copper cube (6 cm^2)

k_{ox} : rate constant for the reaction between an oxidant and copper surface

$[Ox]$: concentration of an oxidant, time dependent

n_{e^-} : number of electrons involved in redox process (one electron for HO· and two for H_2O_2)

As the rate constants of interfacial oxidation of copper are unknown it was used the diffusion controlled rate constant that is 10^{-6}m/s.

The results of numerical simulations compared to experimental results are shown in Table 2.3.

Table 2.3 Comparison between calculated amount of oxidized copper and measured amounts of dissolved copper

Experiment	Dose rate [Gy/h]	NUMERICAL SIMULATION Oxidized copper [µmol/m^2]	EXPERIMENTAL RESULT Dissolved copper [µmol/m^2]
3)	80	34	1416
4)	770	7	917

The results from the numerical simulations, which evaluate the amount of oxidized copper, are a way much lower than the experimental dissolved copper results. The discrepancy is even higher if it is taken into account that ICP analysis only evaluates the amount of copper dissolved in water and it does not take into account the amount of oxidized copper of the surface.

The only agreement among the two results regards the effect of dose rate: lower dose rates give higher level of oxidation, considering a same total dose.

The huge difference between the experimental and numerical analysis shows that in the radiation induced corrosion there are others radiation driven processes instead of aqueous radiolysis. The influence of the water radiolysis seems to be insignificant in the process of

radiation induced corrosion. There should be others reactions involved between the copper surface and the aqueous system subject to gamma irradiation that are still unknown.

The aim of this work is to investigate further the mechanism of reactions that occur at the surface between the pure copper metallic surface and the products of gamma irradiation.

Chapter 3

Irradiation experiments and catalytic decomposition of H₂O₂ on different materials

The first experimental session planned involved some materials taken into account in the KBS-3 concept for the storage of the spent nuclear fuel: iron, stainless steel and copper. An irradiation session was carried out in order to better understand the relation between the irradiation effects on the dissolution of metals in solution. Afterwards the kinetics of decomposition of hydrogen peroxide on the surfaces of these materials was evaluated, this species is considered the most important oxidant product of the radiolysis of water due to irradiation.

3.1 Studies on dissolution of irradiated metals

The first study was planned in order to better understand the effects of gamma irradiation on surfaces of materials, it was performed with metals especially used in the SKB repository project. The copper canisters of the KBS-3 concept is designed with iron inserts so the materials analyzed in the first irradiation experiment were iron, in different shape as pieces and powder, iron oxide and stainless steel pieces.

The stainless steel was chosen for its corrosion resistance properties, so that it was possible to evaluate and compare the effects of the irradiation on materials with significant different properties.

The second run considered powders of iron, stainless steel and copper oxides (tenorite and cuprite powders). The copper oxides have a crucial role in the understanding of the effects of radiation induced corrosion of copper. The ICP analysis could not get valid results from the oxides of copper so that another run was performed with these powders in order to retest them, together was also used the copper powder.

3.1.1 Irradiation experiments on different materials

The gamma irradiation used in irradiation experiments was performed with the MDS Nordion 1000 Elite Cs-137 gamma source. In order to expose more samples at one time at a same irradiation session, it was arranged an eight-positions sample holder. This holder was then inserted in a vessel which is introduced directly inside the gamma source. The vessel is a metallic cylinder which has a mark that corresponds to the positions U-3 and L-3 and a front insertion in the gamma source. A depiction of this tool can be seen in the Figure 3.1
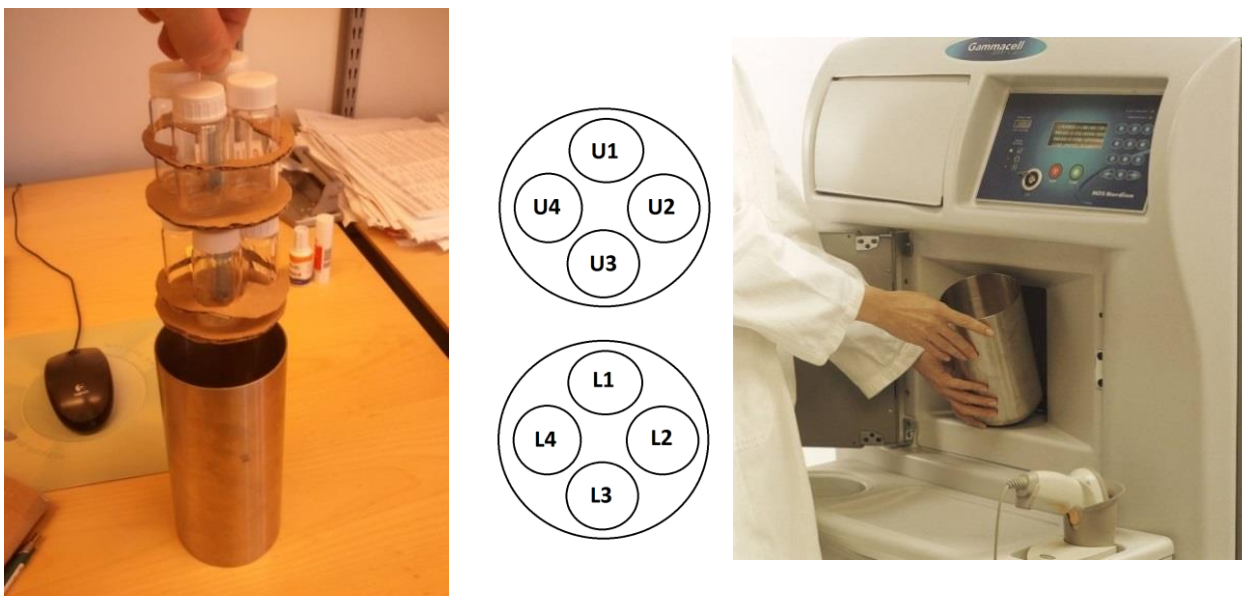
Figure 3.1 Sample holder with 8 glass vessel positions, 4 positions each level (U : upper level, L : lower level), representation of the insertion of the holder inside the gamma source

The vessel is introduced inside the gamma source instrument in a frontal position (Figure 3.1), after setting the time of irradiation and press start, the cylindrical vessel rotates from the position of insertion until it reaches the place directly in front of the gamma source of Cs-137. The metallic cylinder contains eight glass vessels, as it is not able to turn on itself the two glass vessels in position L3, U3 are exposed to the highest doses, while the positions directly behind these, L1 and U1, are shielded and they receive the lowest doses (see Figure 3.2).
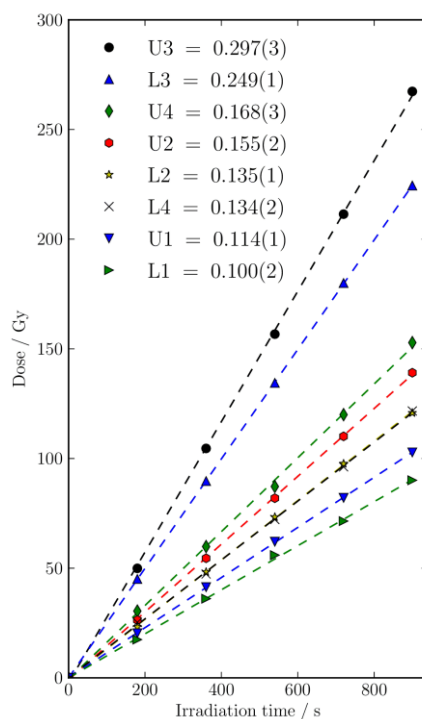

Figure 3.2 Fricke dosimeter analysis for the evaluation of the dose rates at which the 8 glass vessels of the holder are exposed to (U: upper level, L: lower level , 1- 4: positions, see Figure 3.1).

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The dose rates, at which every position of the 8-positions holder is exposed to, have been evaluated by the Fricke dosimetry. The data obtained with this analysis are shown in the figure 3.2.

3.1.1.1 Experimental details

The studies on different materials were performed in few irradiation sessions.

Each irradiation session involves samples of different materials immersed in a solution of 10 ml of deaerated Millipore Milli-Q water enclosed in glass beakers. All the metals used were cleaned in a UV ultrasonic bath or sampled in a protected inert atmosphere before been placed in the glass vessel filled with 10 ml of water. The insertion of the samples in the beakers was done inside a glove box in order to maintain anoxic conditions. The glass vessels were then sealed thanks to the use of Parafilm around the lid.

For each material were prepared three samples with the same procedure, the purpose is to expose two samples at the irradiation and compare the results of them with a reference sample. The reference samples were stored during the period of the irradiation at room temperature covered with aluminum foil. The irradiation of the samples in the gamma source is carried out at room temperature.

The materials exposed to irradiation were: iron chips of irregular shape, 99,98%(metal basis)(ALDRICH) and stainless steel AISI 304 pieces (GoodFellow). Then different kinds of powders analyzed were: iron powder ≥99%, powder (fine) (ALDRICH), ferric oxide powder < 5µm (CAS[1309-37-1])(≥99% SIGMA-ALDRICH), stainless steel AISI 316-L powder MESH 100 (Alfa Aesar), copper (II) oxide powder (CuO) < 50 nm (CAS [1317-38-0])(99,99% ALDRICH),copper (I) oxide powder (Cu_2O) (CAS[1317-39-1]) (ALDRICH) and copper powder MESH -100+325 (CAS [7440-50-8])(99,9% AlfaAesar).

The materials used in the first session were iron pieces, stainless steel in a powder form and then two copper oxides powders: the copper (I) oxide, cuprite, and the copper (II) oxide, the tenorite were tested.

A summary of the materials and samples analyzed is presented in the table below.

Table 3.1 First irradiation session characteristics: 114 hours of exposition, the materials involved are powders and iron pieces.

SAMPLE	MASS (gr)	POSITION OF THE SAMPLE	DOSE RATE (Gy/s)	IRRADIATION TIME (h)	TOTAL DOSE (kGy)
1) IRON PIECE	0,631	L1	0,100	114	41
2) IRON PIECE	0,641	L2	0,135	114	55
3) IRON PIECE	0,599	REFERENCE	0	114	0
4) SS POWDER	0,506	L3	0,249	114	102
5) SS POWDER	0,506	L4	0,134	114	55
6) SS POWDER	0,502	REFERENCE	0	114	0
7) TENORITE	0,109	U1	0,114	114	47
8) TENORITE	0,106	U2	0,155	114	63
9) TENORITE	0,108	REFERENCE	0	114	0
10) CUPRITE	0,111	U3	0,297	114	122
11) CUPRITE	0,113	U4	0,168	114	69
12) CUPRITE	0,112	REFERENCE	0	114	0

The choice of the amount of powder to use in each sample is related to the size of the powder. As the tenorite and cuprite have a small particle size, the tenorite is indeed a nanopowder, the samples were prepared with a lower amount of powder compared with the copper samples in order to get a roughly similar volume.

The second irradiation session was carried out with samples of different powders: stainless steel, copper, tenorite and cuprite. The materials considered are mainly the same of the first irradiation except for the copper. The stainless steel had in the previous analysis some relevant results that were rechecked with the third irradiation. This requirement was due to the fact that the very low value of the ICP results could have been only due to measurement uncertainty. The tenorite and cuprite had not relevant results because of a lack in the filtration process, so they were retested even in the third session. The copper powder was chosen because of the peculiar importance of this material in the studies presented in the next chapters.

The scheme of the second irradiation session can be seen in the Table below.

Table 3.2 Second irradiation session characteristics: 120 hours of exposition, all the materials involved are powders.

SAMPLE	MASS (gr)	POSITION OF THE SAMPLE	DOSE RATE (Gy/s)	IRRADIATION TIME (h)	TOTAL DOSE (kGy)
1) SS POWDER	0,518	L3	0,249	120	108
2) SS POWDER	0,519	L4	0,134	120	58
3) SS POWDER	0,514	REFERENCE	0	120	0
4) COPPER	1,517	L1	0,100	120	43
5)COPPER	1,519	L2	0,135	120	58
6) COPPER	1,517	REFERENCE	0	120	0
7) TENORITE	0,108	U1	0,114	120	50
8) TENORITE	0,110	U2	0,155	120	67
9) TENORITE	0,106	REFERENCE	0	120	0
10) CUPRITE	0,113	U3	0,297	120	129
11)CUPRITE	0,118	U4	0,168	120	73
12) CUPRITE	0,117	REFERENCE	0	120	0

The glass vessel samples taken out from the gamma source presented a darkened surface that is a typical transformation due to the interaction between the irradiation and the oxygen and silicon atoms of the glass.

The solution of water of each sample irradiated and of each reference was then prepared for the analysis at the ICP.

3.1.2 ICP analysis

The Inductively Coupled Plasma technique is a powerful technique that is able to reach really low detection limits (order of ppm and ppb). It is widely used for the analysis of dissolved elements in aqueous solutions.

The reaction solutions of each sample were analyzed thanks to this spectroscopic measurement after a filtration process. The solutions were analyzed after the removal of the solid particles with a 0,2 μm filter. The trace elemental analysis were carried out with a Thermo Scientific iCAP 6000 series ICP spectrometer.

The elements investigated in all the experiments presented are Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn) and Nickel (Ni). All the metals, except copper, are analyzed using an ICP multi element standard while the copper analysis is carried out with a single standard, that realizes a more accurate evaluation.

The results obtained from the samples of the first and the second irradiation are presented in the tables below.

Table 3.3 First irradiation session analysis: ICP results rounded to 2 decimal places.

SAMPLE	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	TOTAL DOSE (kGy)
1) IRON PIECE	-	-	0,01	3,63	1,65	-	41
2) IRON PIECE	-	-	0,01	2,47	0,85	-	55
3) IRON PIECE	-	-	-	0,90	0,01	-	0
4) SS POWDER	0,01	-	0,16	0,01	0,07	1,14	102
5) SS POWDER	0,01	0,02	0,01	0,07	0,06	1,08	55
6) SS POWDER	-	0,01	-	0,05	0,02	0,22	0
7) TENORITE	-	-	37,23	-	-	0,02	47
8) TENORITE	-	-	37,33	-	-	0,03	63
9) TENORITE	-	-	35,32	-	-	0,03	0
10) CUPRITE	-	-	41,88	-	0,02	0,01	122
11)CUPRITE	-	-	33,08	-	0,02	0,01	69
12) CUPRITE	-	-	36,46	-	0,02	0,01	0

From the results showed above is clear that the dissolution of iron increases after an exposition to gamma irradiation. The amount of dissolution is roughly three times higher in the irradiated samples, in the irradiated solutions were present even red particles dispersed that were not present in the reference. This is due to a process of oxidation. The releases involve even amounts of Manganese.

The stainless steel presents a slightly higher dissolution of mainly Manganese and Nickel due to irradiation, even if the values are really low this trend was rechecked in the second irradiation session, see Table 3.4.

The analysis of tenorite and cuprite reveals a high amount of particle dissolved in solution. The high amount of particles dissolved cannot be related to any irradiation process because also the reference samples show large amount of particles dissolved in solution.

The solubility of Tenorite and Cuprite was checked with the results obtained from the ICP analysis: as they present a solubility of respectively 30 and 3 μM [19] it means that the solubility of tenorite and cuprite in pure water at room temperature is converted into 2,39 and 0,43 ppm. This means that the amount of copper dissolved in the analyzed solutions depends on particles dispersed and not well filtered, as the reference samples should only present an amount of copper dissolved due to the solubility limit.

The second irradiation was carried out with the tenorite end cuprite again, the purpose is to use a much thinner filter trying to avoid particles dispersed in solutions.
The results from the second irradiation session are presented in the table below.

Table 3.4 Second irradiation session analysis: ICP results rounded to 2 decimal places.

SAMPLE	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	TOTAL DOSE (kGy)
1) SS POWDER	-	-	0,04	-	0,06	0,84	108
2) SS POWDER	-	0,03	0,02	0,01	0,07	0,87	58
3) SS POWDER	-	-	-	-	-	0,13	0
4) COPPER	-	-	5,74	-	-	0,01	43
5) COPPER	-	-	6,25	-	-	0,01	58
6) COPPER	-	-	0,25	-	-	-	0
7) TENORITE	-	-	32,12	-	-	0,03	50
8) TENORITE	-	-	34,34	-	-	0,03	67
9) TENORITE	-	-	30,14	-	-	0,02	0
10) CUPRITE	-	-	37,36	-	0,02	0,01	129
11)CUPRITE	-	-	38,07	-	0,02	0,01	73
12) CUPRITE	-	-	35,55	-	0,02	0,01	0

The filtration of aqueous samples of tenorite and cuprite was performed both with the filters of 0,2 μm size and with thinner filters of a size of 0,02 μm. In the table 3.4 are presented only the results from solutions filtered with the thinnest filters. There was no relevant difference between the results evaluated by ICP on the solutions filtrated with the 0,2 and the 0,02 μm filters. In order to investigate the effect of irradiation in these two oxides powders samples, the solutions were further analyzed with a PCCS (Solid Particle Counter) but it was not possible to detect the amount of particles in solution. The detection limit of this tool is much higher than the ICP one. As the importance of tenorite and cuprite is quite relevant in the studies of radiation induced corrosion of copper, it was then performed a severe session of centrifugation in order to try to separate the thinner particles from the biggest ones and provide experiments with a filterable medium size powder. After ten centrifugations at high speed of samples of powders and MilliQ water, the solutions presented a reasonable level of ppm dissolved at ICP (all the solution analyzed presented levels of Copper dissolved in water lower than 2 ppm for tenorite, while for cuprite the results were between 0,5 and 5 ppm). The centrifugation can work with these nanopowders in order to reach an average particle size big enough to allow the analysis of the solutions at the ICP. The problem is the impossible way to dry or weigh the amount of powders after the centrifugation as during the pouring out of the

old aqueous solution is not quantifiable the amount of powder pour out. As there is no method so far to weigh the powder after the centrifugation,it is no possible to perform experiments at a known amount of powder. The experiments performed with tenorite and cuprite need a mass comparison in order to evaluate the first-order rate constant as a function of the mass value obtained at initial fixed concentration of hydrogen peroxide. Due to this requirement, all the aqueous solutions used in these experiments were not analyzed with ICP as this analysis has no validity.

3.2 Catalytic decomposition of H_2O_2 on metallic surfaces: iron, stainless steel and copper

The hydrogen peroxide is the most important oxidant species produced by the radiolysis of water due to irradiation. The purpose of H_2O_2 experiment is to investigate and compare the influence of hydrogen peroxide as main cause of radiation induced corrosion on different metallic surfaces involved in the KBS-3 project at the same conditions of the repository, that is an aqueous anoxic environment. In order to investigate this oxidant in contact with the chosen materials a number of experiments at same conditions were performed. The anoxic characteristic of the aqueous environment was performed with a continuous purging of the solution with an inert gas. The oxidant product produced by the radiolysis of water due to irradiation was simulated in the experiments adding in the system a desired concentration of hydrogen peroxide.

The evaluation of the concentration of hydrogen peroxide in solution was carried out with a spectrophotometric analysis that is better known as the Ghormley method. A brief description of this method and of the experimental analysis made on iron, stainless steel and copper follows in the following paragraphs.

3.2.1 Ghormley method

The method used to evaluate the hydrogen peroxide consumption in the aqueous solutions is called Ghormley triiodide method, a spectrophotometric method.

Thanks to this spectrophotometric analysis it is possible to estimate the concentration of H_2O_2 in the system as a function of reaction time. The sample to be analyzed is extracted from the reaction vessel at a certain time, then is further inserted in a cuvette in which are added a solution of potassium iodide and a catalyst. The characteristics of the solutions are: potassium iodide 1M made from potassium iodide powder dissolved in Millipore MilliQ water, the catalyst is a solution 1M of sodium acetate (NaAc) / 1M of acetic acid (HAc) plus few drops of ammonium molybdate $((NH_4)_2Mo_2O_7)$.

When these solutions are added in the cuvette together with the sample, a yellowish solution comes out. In order to evaluate the concentration of hydrogen peroxide in the sample is used the Ghormley method which is a spectrophotometric method.

The absorbance of the sample is evaluated with the WPA Biowave II or a Jasco V-630 UV/vis spectrophotometers. The cuvette that is analyzed by the spectrophotometer contains 2 ml of solution with this composition:
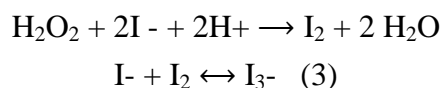
1.6 ml H_2O (Millipore MilliQ water)

0.2 ml sample taken from the reaction vessel

0.1 ml KI solution

0.1 ml catalyst

The concentration of H_2O_2 is measured by UV visible spectrophotometry. The absorbance of the compound analyzed by the spectrophotometer is the triiodide ion that results from this reaction [21]:

$$H_2O_2 + 2I- + 2H+ \longrightarrow I_2 + 2\,H_2O$$
$$I- + I_2 \longleftrightarrow I_3- \quad (3)$$

The absorbance of I_3- is evaluated at a wavelength of $\lambda = 355$ nm which corresponds to the maximum absorption for the triiodide ion. The concentration of the hydrogen peroxide can be evaluated via the Beer – Lambert´s equation (4).

The absorbance related to the triiodide ion can be related directly with the concentration of H_2O_2 in solution through this equation:

$$A = b \cdot \varepsilon \cdot c \quad (4)$$

Where A is the measured absorbance, b is the path length, ε is the wavelength dependent molar absorptivity coefficient (M^{-1} cm^{-1}) and c is the analyte concentration. The coefficients b and ε are considered constants so the absorbance measured by the spectrophotometer is directly proportional to the concentration of the triiodide ion.

Thanks to a calibration curve previously made on this model for this system it has been found that there is a linear correlation between the absorbance of the triiodide ion and the concentration of H_2O_2. The recorded time at which the concentration of H_2O_2 is plot is the exact sampling moment, that is the moment of the extraction of the sample with the pipette from the reactor vessel. The samples are then analyzed with the spectrophotometer as soon as possible in order to detect the concentration of H_2O_2 only few minutes after the sampling.

The materials investigated are metallic pieces of iron, stainless steel discs and copper in different shapes. The results are shown in the following paragraph.

3.2.2. Experimental Details

The metals studied were iron chips of irregular shape 99,98% (metal basis) (ALDRICH), stainless steel AISI 304 pieces (GoodFellow) and copper cubes cut from a SKB copper canister wall (99,992% Cu, major impurities are Ag and P).

The samples were stored in an inert atmosphere: they were not contaminated or oxidized, each sample was then put in a glass beaker filled with 50 ml Millipore MilliQ water solution at a concentration of 0.5 mM of H_2O_2.

All the different materials were put in contact with solutions at the same hydrogen peroxide concentration in order to compare the effects of this species in contact with materials with different corrosion resistance properties. The solutions of diluted hydrogen peroxide were weekly prepared from a 30% standard solution (Merck) stored in a fridge. This procedure avoid the degradation of hydrogen peroxide.

The evaluation of the decomposition of hydrogen peroxide on metal surfaces in aqueous anoxic systems has been investigated at room temperature with the so called Ghormley method.

All the reactor vessels filled with the diluted hydrogen peroxide solutions are continuously purged with a constant flux of pure nitrogen gas (AGA Gas AB). The gas flow is used in order to perform an inert anoxic atmosphere and also a slight stirring of the solution.

The results are plot in the next paragraph.

3.2.3 Results

The decomposition of hydrogen peroxide on metal surfaces in aqueous anoxic system has been investigated at room temperature in all the following experiments.

The first material investigated was iron, the shape of the metal was in form of pieces put in a glass beaker filled with a 50 ml Millipore MilliQ water solution at a concentration of 0.5 mM of H_2O_2. The iron pieces were previously stored in an inert atmosphere as all the others materials in order to avoiding any contaminations. The sampling of the system was chosen to be every 15 – 30 minutes according to the speed rate of consumption of the hydrogen peroxide. The data obtained are presented in the following graphs.
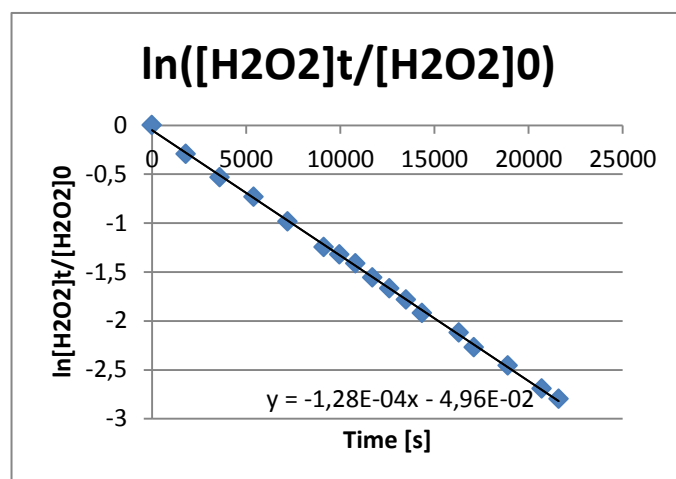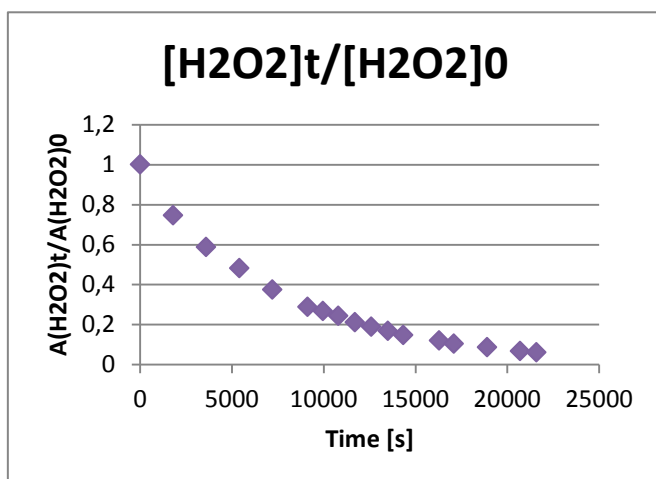
38

Figure 3.3 Iron piece 10 April : normalized concentration of H_2O_2 ($[H_2O_2]_0 = 0.5$ mM) as a function of reaction time, on the right the plot of $\ln([H_2O_2]/[H_2O_2]_0)$ as function of reaction time.

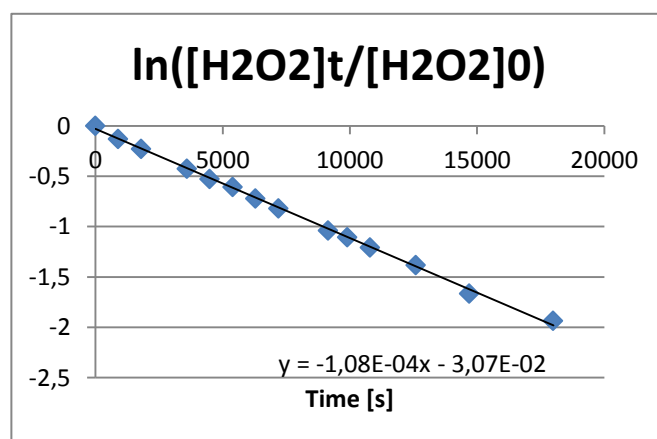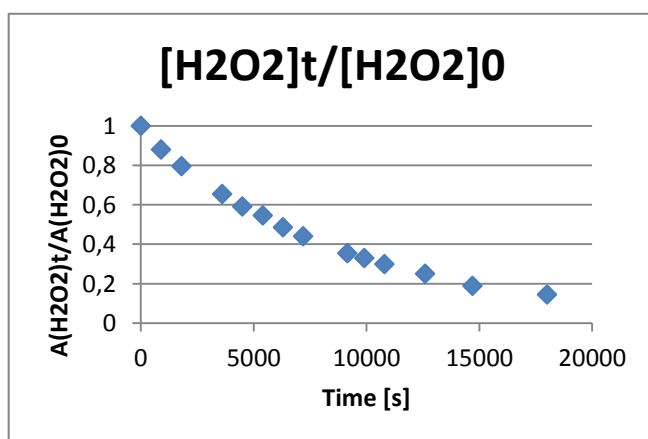**Figure 3.4** Iron piece 11 April : normalized concentration of H_2O_2 ($[H_2O_2]_0 = 0.5$ mM) as a function of reaction time, on the right the plot of $\ln([H_2O_2]/[H_2O_2]_0)$ as function of reaction time.

The aqueous system analyzed is continuously purged with pure nitrogen in order to perform an anoxic condition and a stirring of the solution. The results present the normalized concentration of H_2O_2 : every absorbance value obtained from the spectrophotometer normalized to the background, is then divided by the absorbance of H_2O_2 at the time t=0.

The trend of the consumption of the H_2O_2 makes possible to understand the decay rate and the order of the kinetic of the reaction.

The hypothesis of a first order kinetic law has been investigated thanks to the trend of the obtained data. The plots of $\ln([H_2O_2]_t/[H_2O_2]_0)$ were presented above.

The kinetic of the reaction can be considered as a pseudo first – order reaction for H_2O_2, so the concentration of H_2O_2 is expected to evolve according to:

$$\frac{-d\,[H2O2]}{dt} = k\,[H2O2] \quad (5)$$

$$ln\frac{[H2O2]}{[H2O2]0} = -\,k\,t \quad (6)$$

The equation (5) is further integrated into equation (6).

In the previous formulas k is the pseudo first – order rate constant, t is the reaction time and $[H_2O_2]_0$ is the concentration of hydrogen peroxide at time=0. The k constant has been evaluated thanks to a linear regression analysis, for the first iron piece k is $(12.89 \pm 0.108$)· $10^{-5}\,s^{-1}$ while for the second experiment the k value is $(10.83 \pm 0.112)\cdot 10^{-5}\,s^{-1}$.

After the development of this method with the iron, it has been performed the same experiment with samples of copper cubes. All the samples of copper cubes have the same dimension of 1 cm side and are cut from a piece of the canister that is going to be used in the SKB project for the storage of the spent nuclear fuel.

The results from the experiments follow below.
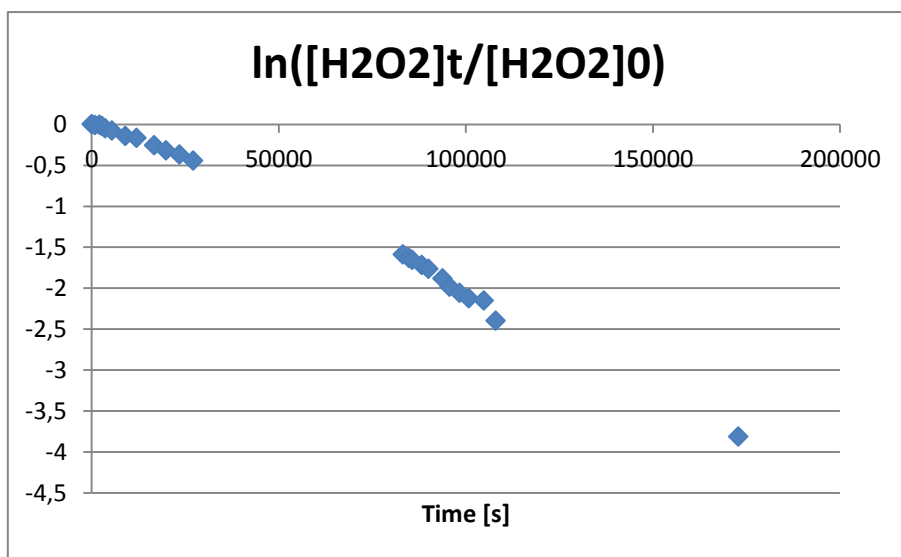
Figure 3.5 Copper cube 17 -19 April : normalized concentration of H2O2 (H2O2 at t =0 , 0.5 mM) as a function of reaction time
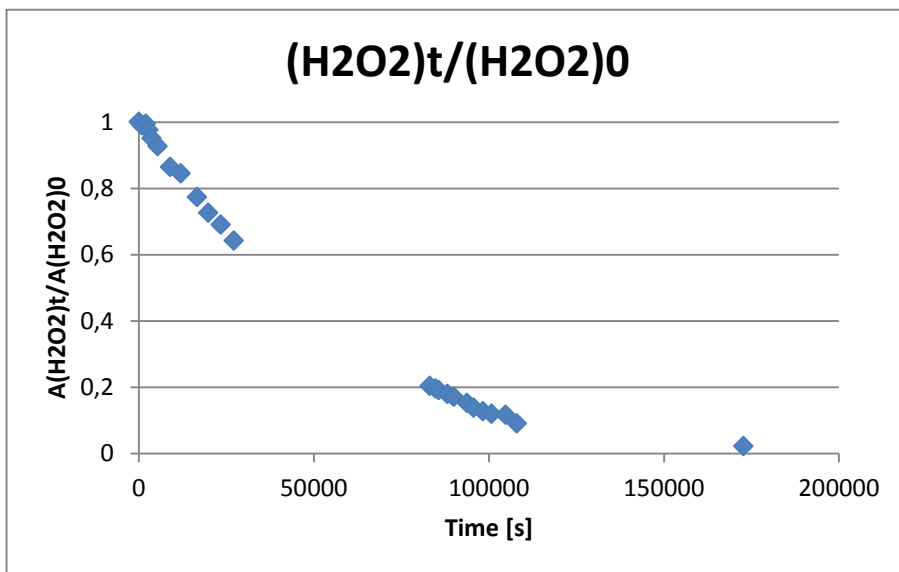
Figure 3.6 Copper cube 17-19 April : plot of $\ln([H_2O_2]/[H_2O_2]_0)$ as function of reaction time.

As it can be seen from the plots of the experiment it is evident that the reaction of the consumption of hydrogen peroxide has a much slower speed rate in the copper cube system compared to the iron experiment. The reaction developed entirely only after 47 hours, so it was not possible to follow the entire trend of the reaction. In order to better understand the behavior of the hydrogen peroxide in contact with the copper cube surface, another experiment at the same conditions was performed in order to try to evaluate the whole kinetic of the reaction of consumption of H_2O_2. The second experiment was performed late in the afternoon instead of the early morning; the purpose of this experimental plan was to follow the reaction in the period of time that was not possible to evaluate during the first experiment. The plot of the data obtained in the second experiment are presented below.
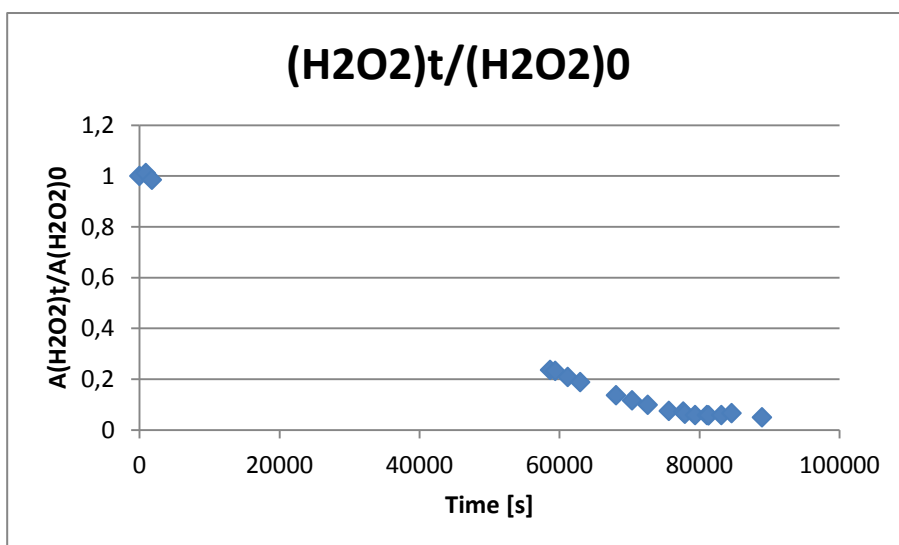

Figure 3.7 Copper cube 18-19 April: normalized concentration of H2O2 (H2O2 at t =0 , 0.5 mM) as a function of reaction time
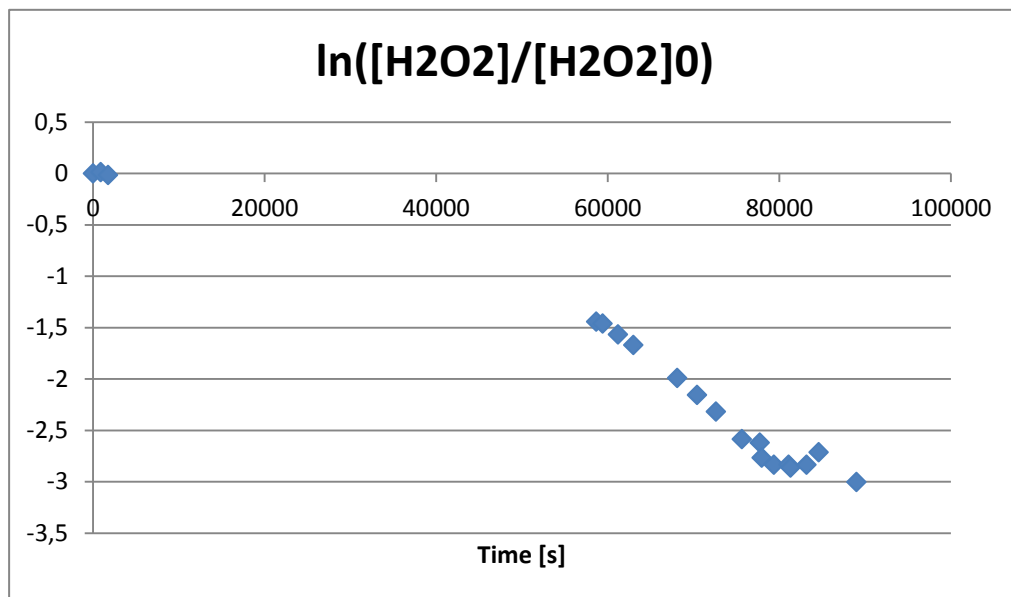
Figure 3.8 Copper cube 18-19 April : plot of ln($[H_2O_2]/[H_2O_2]_0$) as function of reaction time.

The results of the two experiments combined together do not represent the entire kinetics for the hydrogen peroxide reaction. The hypothesis of pseudo-first-order approach cannot explain well the behavior of the decomposition reaction. The reaction that involves the surface of copper cube samples is much more complicated than what was found for the iron piece experiments, therefore it was supposed to perform new experiments even overnight in order to evaluate the whole kinetics of the reaction between H_2O_2 and the copper surface .

After the studies done on the iron pieces and the copper canister's samples, another material was analyzed. From the ICP analysis made on irradiated stainless steel samples, it was shown that this material has much stronger corrosion resistance properties. In order to compare the behavior of this material with the other ones in an anoxic aqueous hydrogen peroxide environment, the same experiment was planned. A stainless steel disc (AISI 304) was used, it was kept into a glass beaker filled with 50 ml of aqueous solution of 0.5 mM of H_2O_2 for almost 72 hours, some samples were analyzed but the values of absorbance were constant during the whole period. This means that the H_2O_2 is not able to react and be decomposed on the surface of the stainless steel that is therefore not corroded.

As it was previously demonstrated by the analysis of metals irradiated at ICP, the stainless steel has high corrosion resistance properties.

Chapter 4

Copper powder: studies on kinetics of decomposition of H$_2$O$_2$ and formation of hydroxyl radical

The first material to be fully investigated in this work is the copper metallic powder. In this chapter all the experiments involving this material are presented. The analysis performed has the purpose of evaluating the kinetics of consumption of hydrogen peroxide and the role of hydroxyl radical as the main product formed during the catalytic decomposition of H$_2$O$_2$ on copper surface. The metallic copper in shape of powder is a flexible compound which allows the planning of many experiments at various conditions.

4.1 A study of the catalytic decomposition of H$_2$O$_2$ and formation of hydroxyl radical on the surface of copper powder

From previous studies [12] was shown that the energy barriers and the pre exponential factors differ widely in the reactions involved in the mechanism of decomposition of hydrogen peroxide on different metal surfaces. This different behavior among various materials means that each surface can present a distinct interfacial/surface process that is characteristic of the oxide surface.

In the mechanism proposed in which the H$_2$O$_2$ reacts on metal oxide surfaces the main reactions take place on the liquid phase. The process that is not yet well understood is the influence of the formation of the hydroxyl radical and its role on the further decomposition of hydrogen peroxide at a solid-liquid interface.

The investigation of this proposed mechanism was first made on a system with copper particles suspension. The copper is the most important material that has to be investigated in this work. The form in powder is more suitable for an experimental analysis in which is needed to set some conditions.

The mechanistic study involves the evaluation of the rate of formation of HO$\cdot$ during the decomposition of hydrogen peroxide in a copper powder suspension and compares its kinetics with the consumption rate of H$_2$O$_2$ in the system. In this manner it should be possible to understand which role and which are the most important reaction pathways that involve the formation of HO$\cdot$.

The hydroxyl radical is a really unstable species, the way used in this work in order to detect the concentration of this radical as a function of reaction time is an indirect method. The method used for the detection of the hydroxyl radical in the system is called Modified Hantzsch Method, a brief description of it is presented in the following paragraph (see 4.2 paragraph).

The method consists in the detection via spectrophotometric measurements of the concentrations of formaldehyde, CH_2O, that is formed by the Hantzsch reaction. This reaction involves a molecule of hydroxyl radical that reacts with a molecule of a scavenger, in this work was chosen as scavenger a methanol solution, which are further transformed into a molecule of formaldehyde and a radical species. In the reaction the amount of hydroxyl radical consumed is directly proportional to the amount of formaldehyde produced considering the stoichiometry of the reaction. During this process the reaction of the hydroxyl radical with methanol can take place only in one position for producing the formaldehyde molecule, but of course the molecules can react in a different way producing others compounds not detectable by the Modified Hantzsch method. In order to evaluate the chemical yield of the reaction involving the HO· and methanol, a calibration method is required. This method consists in quantifying the amount of formaldehyde produced in a system in which is present a known concentration of hydroxyl radical. The known amount of HO· dissolved in the system is produced by γ radiolysis, the hydroxyl radical concentration is given by the radiation chemical yield for this species that is $G_{HO.} = 0.28$ μmol/J [22], considering a system of pure gamma irradiated water with a pH= 4 – 9.

Thanks to the equation (7) is possible to correlate the absorbed dose with the concentration of hydroxyl radicals produced in the system.

$$[HO·] = D \cdot G_{HO.} \cdot \rho \quad (7)$$

where D is the absorbed dose (Gy), $G_{HO.}$ is the radiation chemical yield for HO· (μmol/J) and ρ is the density of the solvent considered (kg/m^3), in this case pure water.

A calibration curve is necessary in order to detect the chemical yield of the method, indeed the real amount of HO· in the system that reacts with methanol producing formaldehyde is not known.

Many different solutions at different concentrations of hydroxyl radical have to be made in order to validate the calibration method; all these solutions react with a methanol solution at a fixed concentration, furthermore the formaldehyde concentrations produced in the system are detected. This calibration method is not yet available, the experimental plan is still ongoing and gives so far a yield for the method of roughly 40 – 60 %. This percentage value represents the concentration of CH_2O produced in relation with the accumulated concentration of HO· in the system that reacts with methanol.

All the experiments presented in this work which involve the Modified Hantzsch Method analysis will show only the formaldehyde concentrations produced in the system because it is not yet known the exact yield of the method, so it is not yet possible to convert the formaldehyde concentrations in hydroxyl radical ones.

The method used is furthermore not able to discriminate whether the HO· is trapped on the surface of the metal or dissolved in solution when the methanol scavenges it. It was proved in any case that the system with the scavenger diluted does not affect the reaction rate of the consumption of H_2O_2. There is no interference in the reaction of hydrogen peroxide on the metal surface between the real system and the system with the scavenger dissolved in.

4.2 The Modified Hantzsch Method

The method performed in order to evaluate and verify the formation of HO· as an intermediate species formed during the catalytic decomposition of H_2O_2 on metallic surfaces is the Modified Hantzsch method. The same method has been performed in experiments carried out in the gamma source, in order to evaluate the hydroxyl radical as the main product of the water radiolysis due to radiation.

The method is called modified because is based on a reaction, the Hantzsch reaction, that makes possible the detection of the formaldehyde by spectrophotometric analysis. The modification brought on the Hantzsch method concerns the solutions used. The presence of H_2O_2 in the system prevents the use of acetylacetone or 2,4-pentadione which cause interferences, therefore it has been used acetoacetanilide.

The use of a radical scavenger, in this case methanol, that reacts selectively with the hydroxyl radical makes possible the quantification of this spur. The methanol reacts with HO· producing formaldehyde that is going to be detected by the spectrophotometer; a calibration method is thus necessary to evaluate the exact value of hydroxyl radical produced during the reaction.

This spectrophotometric analysis permits to estimate the concentration of formaldehyde, CH_2O, in the system as a function of reaction time. The sample to analyze is extracted from the reaction vessel at a certain set time, then is filtered with a 0.2 μm filter in order to avoid particles dispersed in the sample and then is further inserted in a cuvette. Inside the cuvette are added two solutions of ammonium acetate and acetoacetanilide. The characteristics of the solutions are: ammonium acetate 4M made by ammonium acetate powder (CAS[631-61-8], Lancaster 98%) diluted in MilliQ Millipore water, acetoacetanilide 0.2 M made dissolving acetoacetanilide powder (CAS [102-01-2], Alfa Aesar > 98%) in pure ethanol.

All these solutions are added in a cuvette together with the sample, this probe is stored in a thermal bath set at 40 °C, the reaction takes place in about 15 minutes and it forms as main product a dihydropyridine derivative, this compound has its maximum absorption wavelength

at 368 nm. Thanks to a calibration curve previously made is then possible to convert the values of absorbance of the dihydropyridine derivative in values of formaldehyde concentrations. The calibration curve gives a linear correlation in the concentration range 0.15 µM to 1 µM in formaldehyde, thanks to this linear coefficient is so possible to convert all the values of absorbance obtained in the experiments in CH_2O concentrations.

The absorbance of the sample is evaluated with the WPA Biowave II or a Jasco V-630 UV/vis spectrophotometers.

The cuvette that is analyzed by the spectrophotometer contains a solution with this composition:

1.5 ml of sample took out from the reactor vessel

2.5 ml of Ammonium Acetate 4 M

1 ml of Acetoacetanilide 0.2 M in ethanol

The probe filled with these solutions has to be kept in a thermal bath set to 313,15 K for 15 minutes. After this period the solution is stirred and poured in a cuvette and analyzed at a wavelength of 368 nm in the spectrophotometer. The absorbance recorded is then converted into a value of concentration of formaldehyde thanks to the calibration curve previously evaluated with the calibration method. The calibration method consists in the comparison of the absorbance of some samples containing 1 ml of acetoacetanilide, 2.5 ml ammonium acetate and 1.5 ml of a sample at a known amount of formaldehyde. The conditions at which the sample is analyzed follow the same procedure used for analyzing the sample taken out from the reactor vessel. Analyzing various samples at a known concentration of formaldehyde it is possible to evaluate a linear correlation among absorbance of the sample and the corresponding concentration of formaldehyde inserted in the sample itself.

The calibration curve used in this conversion is presented in the figure below.
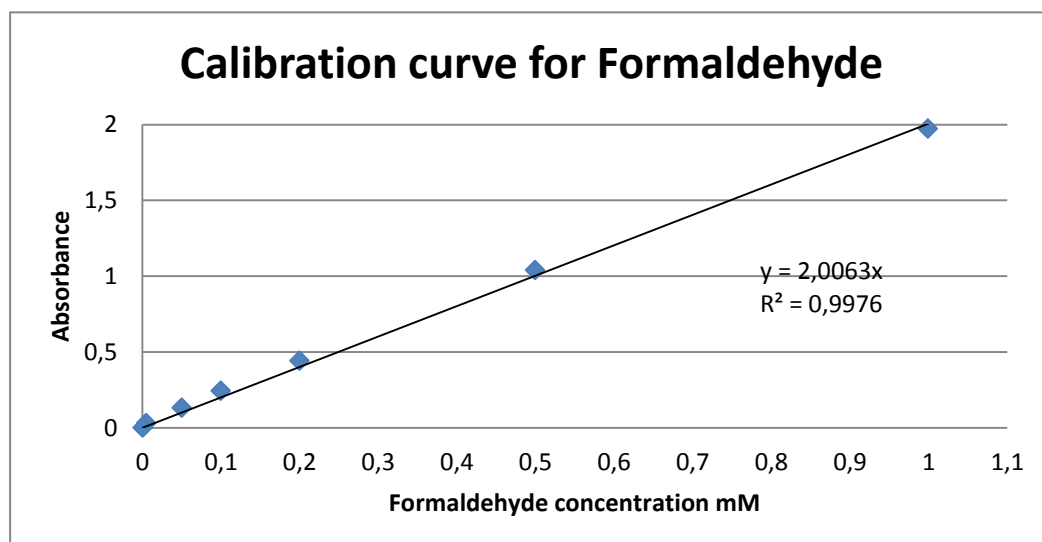

Figure 4.1 Calibration curve for the Modified Hatzsch Method used in this work.

The values of formaldehyde concentration should be then transformed into hydroxyl radical concentration, unfortunately as already said the calibration method is not yet ready. The assumptions formulated in the experiments presented in the following paragraphs and chapters will be concerning the formation of formaldehyde in the system as an evidence of the production of hydroxyl radical.

4.3 Experimental details

The first material used to test the catalytic decomposition of H_2O_2 performing the Hantzsch method is copper in the shape of powder. The material tested is copper powder (MESH -100 +325, (cas[7440-50-8]) (99.9% Alfa Aesar)). The reaction takes place at room temperature in an aqueous volume solution of 100 ml at 5mM concentration of H_2O_2 and at different concentrations of methanol solution.

The experiments were performed with different amount of powder and with various methanol concentrations in order to evaluate the best compromise between reaction time and yield of formaldehyde.

The reactor is a glass baker filled with 100 ml of Millipore MilliQ water solution at a fixed concentration of 5mM of H_2O_2 at different concentrations of methanol that varied from 20 to 300mM. The hydrogen peroxide solutions were prepared in the same way already described in the Ghormley Method paragraph in the previous chapter (see paragraph 3.2.1). All the solutions used in the various experiments in which are used the Ghormley or Hantzsch methods are made with the same procedure.

The main difference that exists in this experimental plan compared to the previous plan described in chapter 3 consists in the concentration of hydrogen peroxide in solution. Here it is inserted a concentration of 5 mM of H_2O_2, that is a concentration 10 times higher than the concentration used in previous experiments. As consequence of this, the Ghormley Method analysis has to be slightly modified. As the concentration of hydrogen peroxide is 10 times higher than in previous experiments, the cuvette which contains the sample and the reactants has to contain a 10 times lower concentration of hydrogen peroxide in order to not provoke interferences with the maximum limit of detection of absorbance of the potassium triiodide in the spectrophotometer.

The cuvette used in the Ghormley Method analysis in all experiments at 5mM H_2O_2 has this composition:

1.78 ml H_2O (Millipore MilliQ water)

0.02 ml sample taken from the reaction vessel

0.1 ml KI solution

0.1 ml catalyst

The system is continuously purged with a constant flux of nitrogen gas (AGA Gas AB) and stirred with a magnetic stirred in order to perform an homogeneous system of powder in solution. The purging of the solution is required for having an inert anoxic atmosphere.

Every sample from the reaction vessel was filtered through a 0.2 μm filter before being inserted in the probe in order to avoid particles in the solution which can influence the spectrophotometric analysis.

In each experiment were performed simultaneously the Hantzsch and Ghormley methods in order to follow at the same time the kinetics of decomposition of hydrogen peroxide and the formation of hydroxyl radical.

4.4 Results

The decomposition of hydrogen peroxide on copper suspension in aqueous anoxic system has been investigated at room temperature in all the following experiments.

First was performed an experimental session in which was tested the efficiency of the scavenger in the system. The purpose of this experimental plan was to evaluate the best compromise between the amount of scavenger diluted and its efficiency in the detection of the formaldehyde formed as product of the Hantzsch reaction. Few experiments were performed with a fixed value of powder but at various amounts of methanol concentration. All the experiments were performed with same conditions in order to compare the results and evaluate the most efficient amount of methanol to use. The smallest value of methanol that will present a high efficiency for the detection of formaldehyde will be used in all the experiments.

The sampling of the system varies in each experiment, it is anyway needed a sampling every 5 – 20 minutes according to the speed rate of consumption of the hydrogen peroxide in each experiment.

Many experiments were performed even at different conditions at the beginning in order to test the system for the first time.

In literature there are no examples about these kind of experiments, after achieving the best conditions to perform experiments at required conditions for this experimental analysis, an experimental plan was set.

Due to the large number of experiments performed, only the plots of some important results are presented below.

4.4.1 Efficiency of the methanol as radical scavenger in the system

The best compromise between amount of radical scavenger to use and formaldehyde yield is evaluated through experiments at same mass powder exposed to different methanol concentrations.
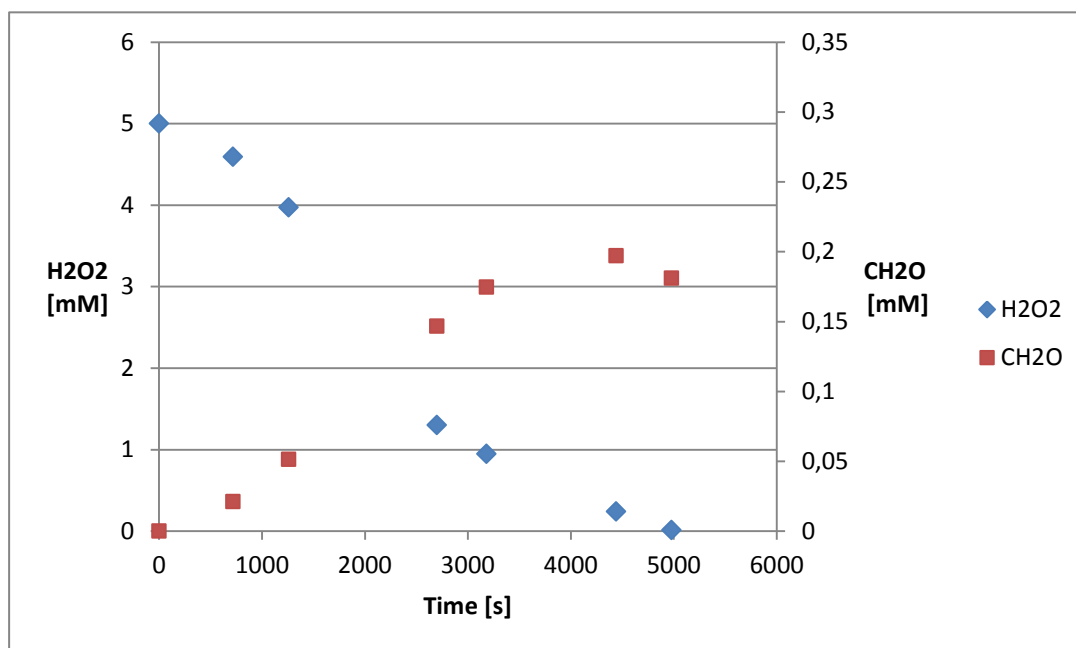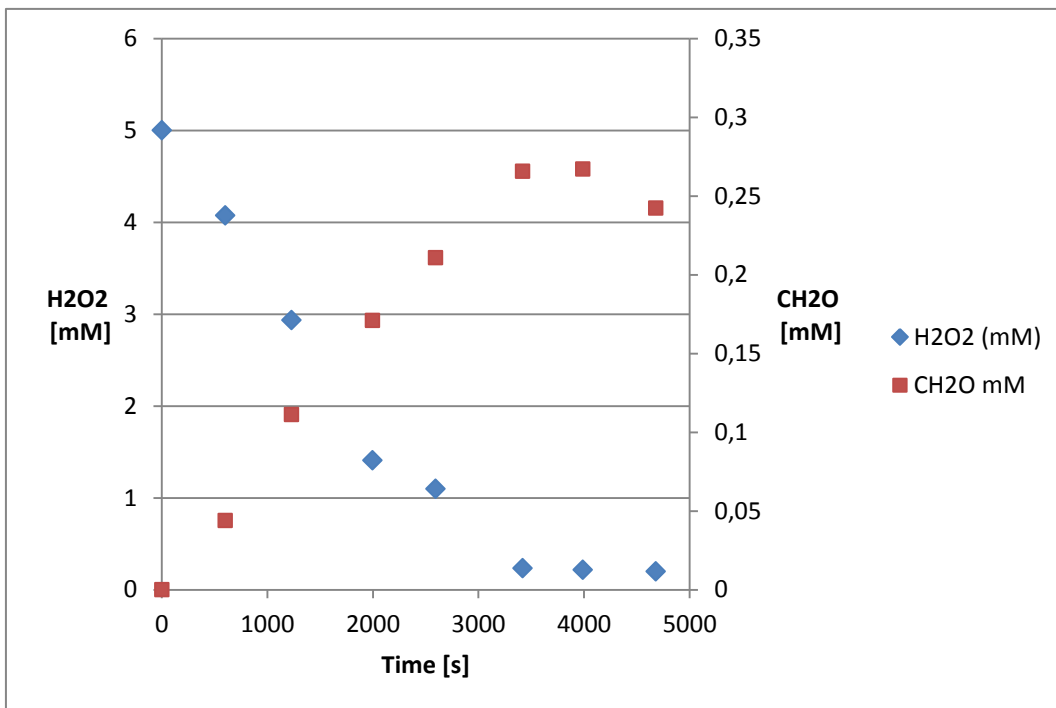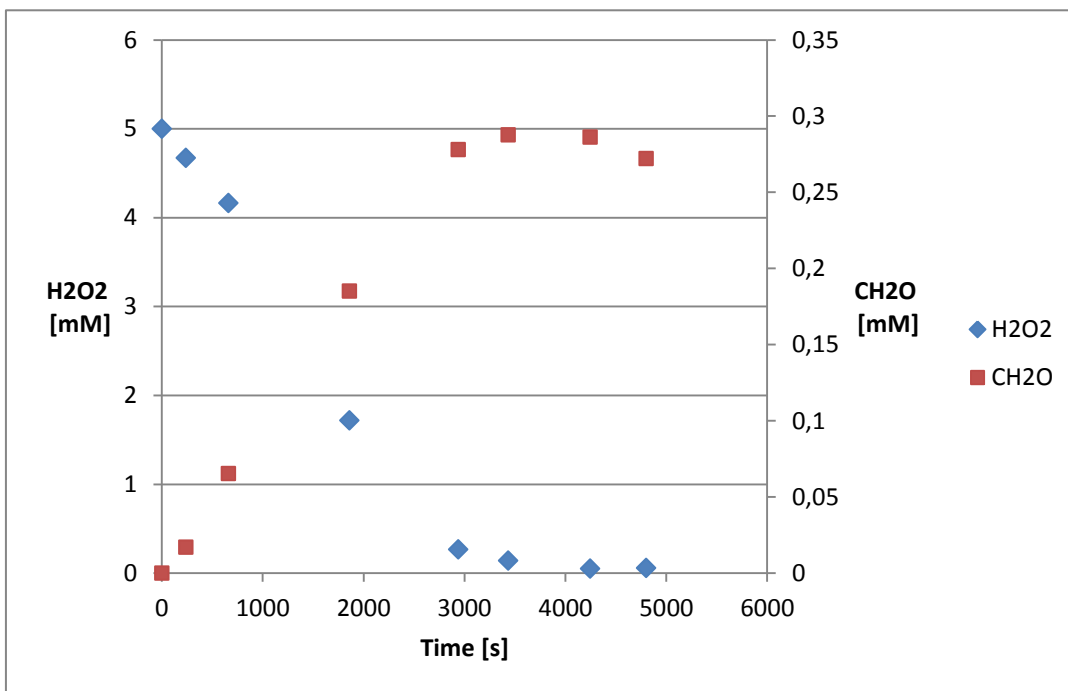

Figure 4.2 Copper powder 1.5 gr (8 May) , CH_3OH 20 mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time

The figures 4.2 – 4.3 – 4.4 show the kinetics of decomposition of hydrogen peroxide and formation of formaldehyde in experiments performed with 1.5 gr of copper powder exposed to different concentrations of radical scavenger, solutions 20mM – 100mM – 200mM of CH_3OH were used.

Figure 4.4 Copper powder 1.5 gr (27 May) , CH$_3$OH 100 mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time

Figure 4.3 Copper powder 1.5 gr (21 May) , CH$_3$OH 200 mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time
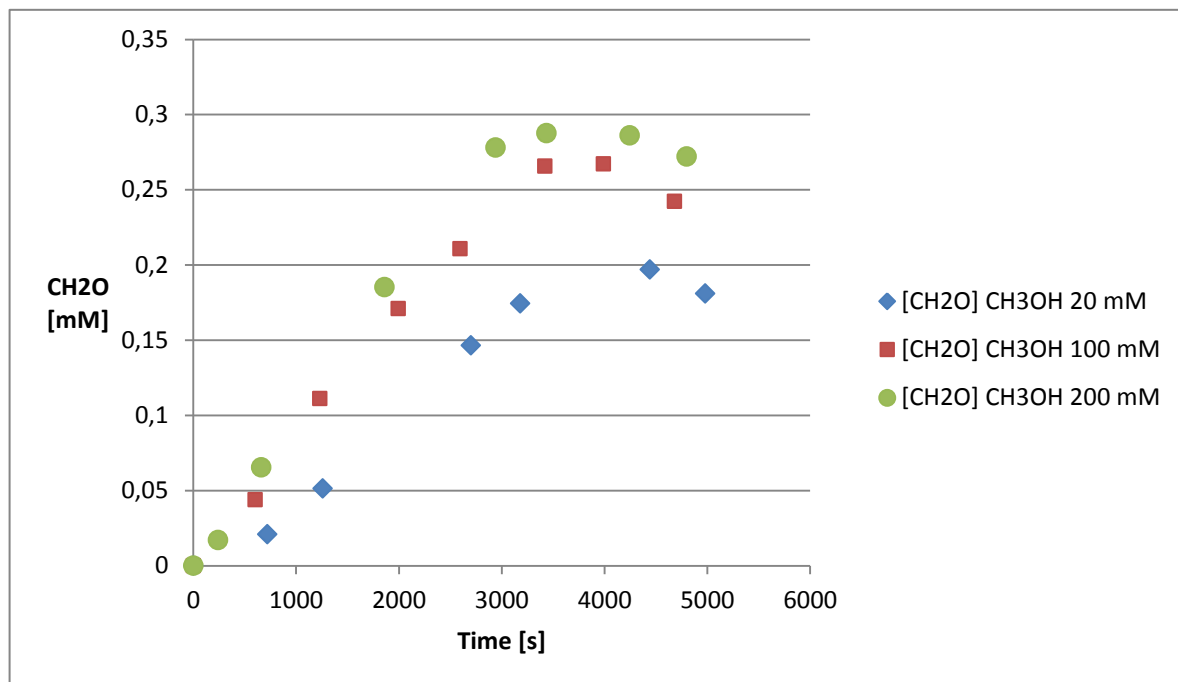
50

Figure 4.5 Evolution in the concentration of CH_2O as a function of reaction time, comparison between different concentrations of methanol solution

In the figure 4.5 is shown the efficiency of methanol as radical scavenger in the copper powder suspension experiment. Each experiment was performed at same conditions and with the same fixed amount of powder, thus all the systems are expected to have the same reactivity and so the same production of HO·. As it can be seen from the plot, the 200mM methanol solution detects the highest amount of formaldehyde while the 20mM methanol solution gives a lower amount of formaldehyde diluted in solution. The experiment performed at 100mM methanol solution gains almost the same amount of formaldehyde detected with the solution at highest concentration of solute. It was previously described that the amount of formaldehyde is directly related to the amount of the hydroxyl radical in the system. As the experiments were performed at same conditions, the concentration of HO· should be the same, the different values detected are a consequence of the action of the scavenger in the system. This means that the 100mM methanol solution is a good compromise for our system among formaldehyde yield and amount of radical scavenger added in the reaction solution. It is better to not introduce useless amount of reactant if is not necessary in the system because it might affect the reactivity of it, for this reason the methanol solution used in all next experiment is the 100mM methanol concentration.

4.4.2 Copper powder suspension experiments

The experiments with copper powder suspensions were performed at various mass amounts and at a set value of reaction solution concentration that is: 5mM hydrogen peroxide, 100mM methanol solution.

All the experiments used for formulating conclusions are presented below. The others experiments performed are collected at the end of this work in the Appendix section.
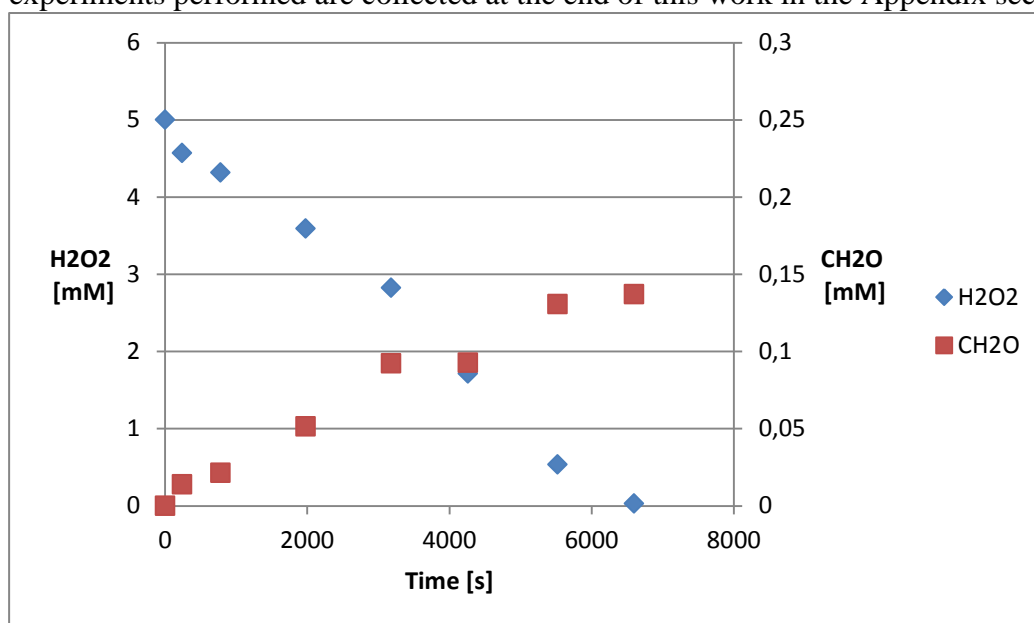

Figure 4.9 Copper powder 1 gr (18 July) , CH_3OH 100 mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time
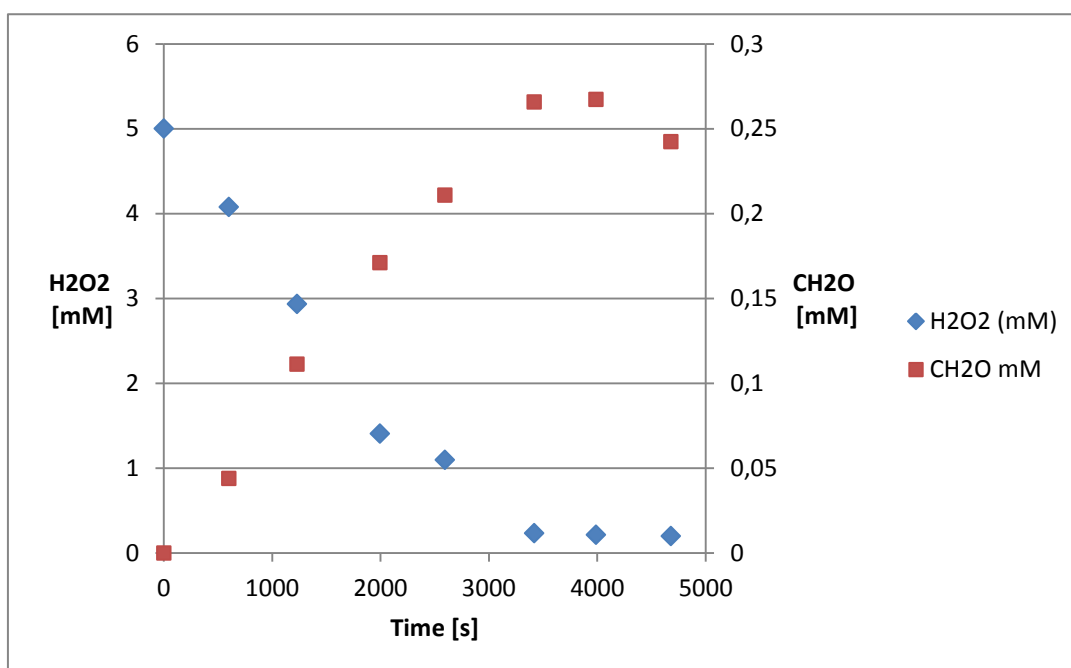
Figure 4.6 Copper powder 1.5 gr (27 May) , CH_3OH 100 mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time
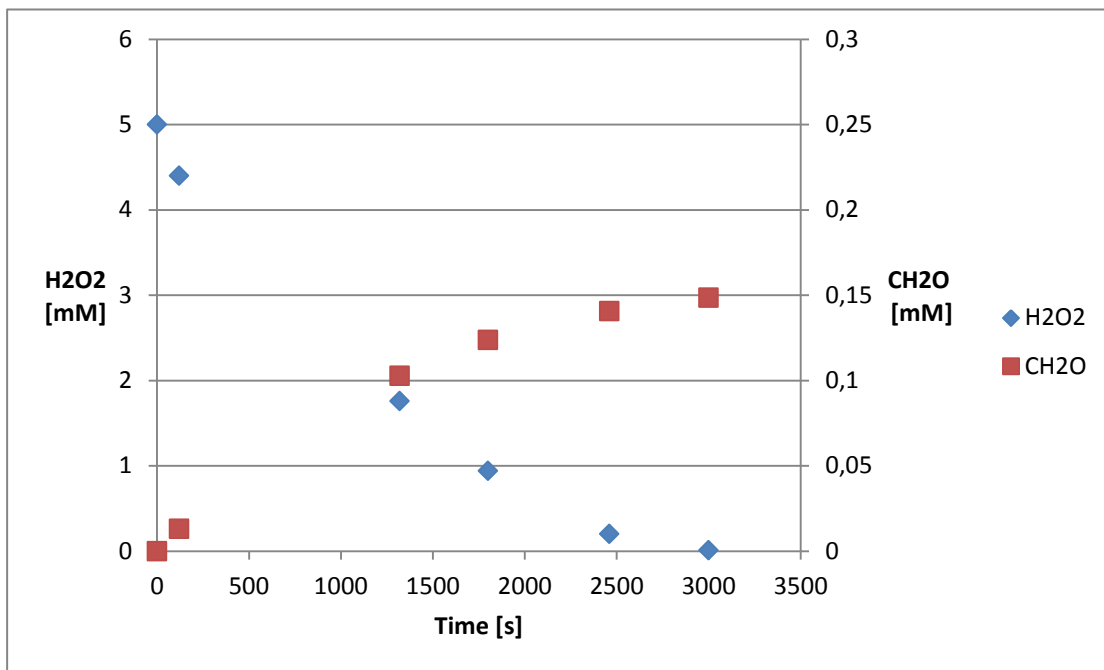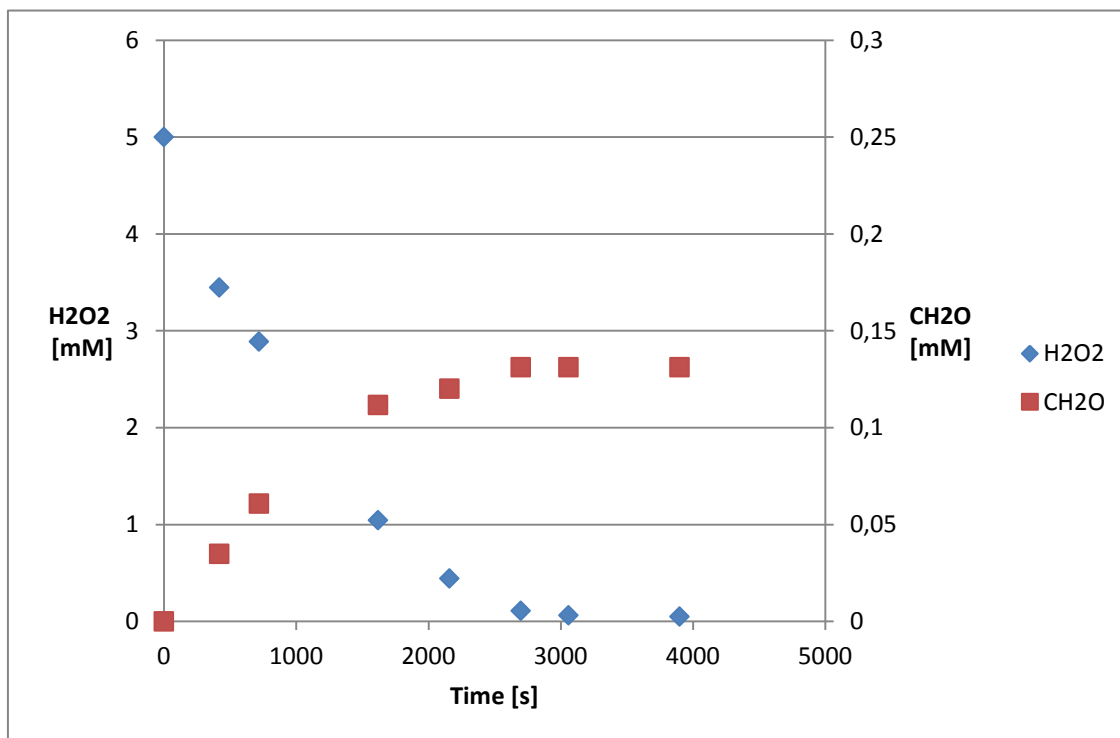
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Figure 4.8 Copper powder 3 gr (17 July) , CH$_3$OH 100 mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time

Figure 4.7 Copper powder 6 gr (5 July) , CH$_3$OH 100 mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time

All the data obtained in the experiments were analyzed with the logarithmic analysis, equations (5) and (6) (see chapter 3, paragraph 3.2.3) in order to evaluate the order of the kinetics of consumption of hydrogen peroxide as it was previously done with the iron pieces. In every case it was not possible to describe the kinetics of the consumption of H_2O_2 as a pseudo first order reaction in the copper suspension system.
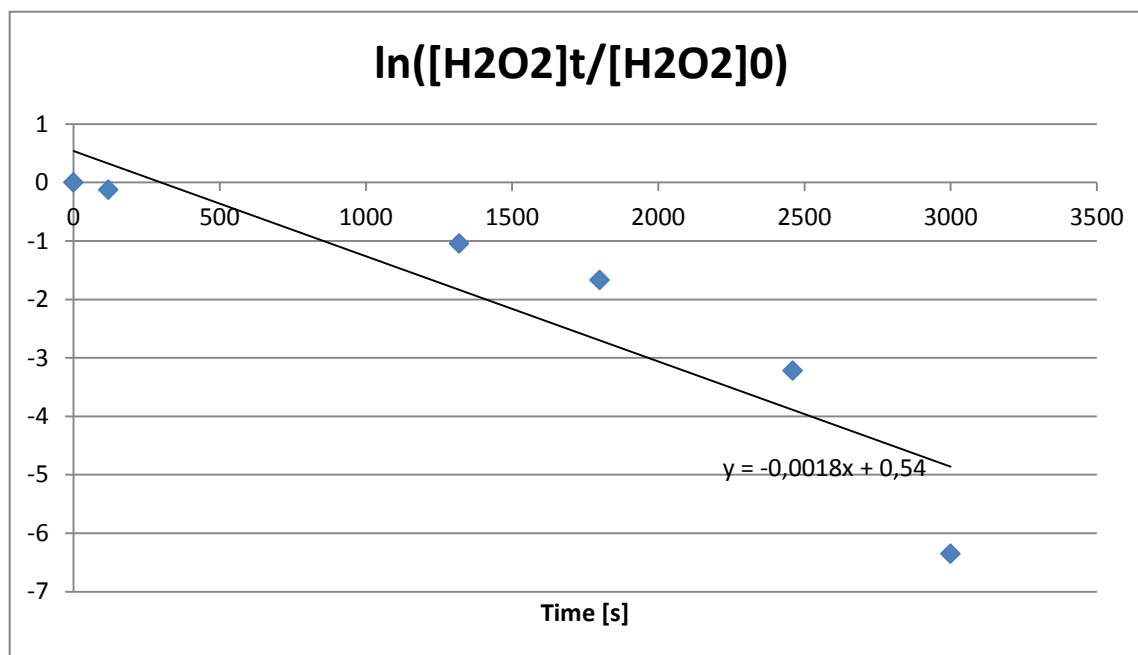

Figure 4.10 Copper powder 3 gr (17 July) , $\ln([H_2O_2]/[H_2O_2]_0)$ as a function of reaction time

As it can be seen in the figure 4.10 a pseudo first order approach cannot describe the reaction pathway that takes place in this system. In every experiment performed the consumption of hydrogen peroxide follows a trend where at the beginning the reactivity is lower than at the end.

The experiments performed cover a wide range of copper mass amounts in order to check if this behavior is a consequence of the saturation process of the surface. In every case the behavior of the system shows the same approach, the reaction speed does not depend on the amount of the powder but on the reactivity of the compound.

The complexity of the reactivity of the system might be related to the different steps involved during the reaction pathway. The copper powder inserted in the reactor is supposed to be pure metallic copper, the copper powder was checked with the XRD analysis and it was proved to be pure metal. During the reaction with hydrogen peroxide the metallic copper reacts into copper (I) oxide and further into copper (II) oxide. The reactivity of the copper in the system changes according to the compounds present as a function of reaction time.

It is of crucial importance to understand the behavior of the single compounds involved in the process first in order to better understand the behavior of the copper powder. For this reason

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an experimental session was planned for investigate the copper oxides behavior in the system. The two oxides are investigated individually in order to discompose the complexity of the copper powder system in many different subsystems. The results achieved are presented in the following chapter.

4.4.3 ICP results

All the reaction solutions involved in the experimental plan were at the end of each experiment filtered and analyzed by ICP (Inductively Coupled Plasma atomic emission spectroscopy) with a Thermo Scientific iCAP 6000 series ICP spectrometer. The purpose of this analysis was to detect the trace elemental analysis in the solutions; as in all the experiments only copper powder was used, the detection of copper was done with a single standard for copper at wavelengths of 213,5 and 219,9. Others elements were anyway checked with a multi element standard IV from Merck that is less accurate compared to the single element standard but still valid.

The results achieved show the presence of only copper dissolved in solution, as was expected. The concentration of copper in solution varies in a range from 1 to 5 ppm. There is no a clear evident trend that relates the amount of copper inserted in the reactor and the copper dissolved in solution. Many experiments were performed and many of them were done at different methanol concentration and at different stirring speed. The highest values of copper concentrations dissolved in solution belong to those experiments at lowest speed of consumption, so that the experiment took a longest time to consume the hydrogen peroxide. The dissolution is then related to the period of time at which the powder is stored in the reaction vessel.
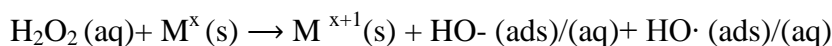
Chapter 5

Studies on kinetics of surface reactions of copper oxides: Tenorite and Cuprite

The mechanism of consumption of hydrogen peroxide on copper surface is not yet a well understood process. The complexity of the reaction kinetics gained over copper powder experiments requires a study in deep on copper oxides, in order to clarify some aspects of the kinetics of copper that was shown to be reaction time dependent.
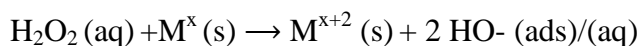
5.1 Investigation on mechanism of catalytic decomposition of H_2O_2 on copper oxides surface

The previous chapter presented the results gained in copper powder experiments about the study of the mechanism of reaction of the hydrogen peroxide on its surface. The kinetics of reaction of this species in contact with copper is not yet well understood as the approximation of a pseudo first order kinetics is not valid. The copper surface in contact with H_2O_2 reacts in a much more complex pathway than what was expected. As it was previously described, the mechanism of consumption of hydrogen peroxide on metal and metal oxide surface follows different pathways as can be seen in mechanism (1) :
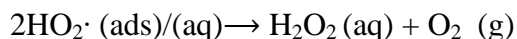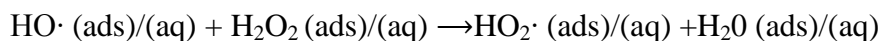
One - electron oxidation:

H_2O_2 (aq)+ M^x (s) $\longrightarrow$ M^{x+1}(s) + HO- (ads)/(aq)+ HO· (ads)/(aq)

Two electron oxidation :

H_2O_2 (aq) +M^x (s) $\longrightarrow$ M^{x+2} (s) + 2 HO- (ads)/(aq)

Catalytic decomposition:

H_2O_2 (aq)+ M ^{y}(s) $\longrightarrow$2HO·(ads)/(aq) +M^y (s)

HO· (ads)/(aq) + H_2O_2 (ads)/(aq) $\longrightarrow$HO$_2$· (ads)/(aq) +H_2O (ads)/(aq)

2HO$_2$· (ads)/(aq)$\longrightarrow$ H_2O_2 (aq) + O_2 (g)

The complex behaviour of the copper suspension system might be due to the reactions involving not only the metallic copper particles but even some others compounds which affect the reactivity of the system. The metallic pure copper can be oxidized into copper (I) oxide and further into copper (II) oxide when the hydrogen peroxide reaches its surface. There are not analytical techniques that are able to characterize the copper powder during and after the experiment in order to detect the composition and the real percentage of oxides produced on the surface. It is anyway proved that the copper undergoes oxidation and consumes the

hydrogen peroxide diluted in solution. The difference in reactivity of the system could be related to the reactivity of the different oxides formed as function of reaction time.

It was previously shown the mechanism of reaction of hydrogen peroxide (1) for a general molecule metal site on the surface; in the case of metal oxide surface the molecule of H_2O_2 can act as an oxidant, as a reductant and can react via catalytic decomposition. The catalytic decomposition that occurs at the interface produce some radical reactive species which can further affect the chemistry and stability of the active surface in contact with the solution.

In order to better understand the kinetics of decomposition of H_2O_2 on copper, an experimental plan that analyse the reactivity of hydrogen peroxide in contact with the copper oxide surfaces was set. The purpose of this study is to evaluate the pathway of the reaction of H_2O_2 on the two copper oxide surfaces. After the estimation of the kinetics of the reactions occurring on the single oxide surfaces, it will be possible to understand if the combination of these two kinetics would explain the overall kinetics of reaction of pure copper surface.

It is known from previous studies that the copper oxidation process produces as the most important and common product the copper (I) oxide, namely the cuprite. Anyway the experimental analysis on copper oxides take into account both the cuprite and tenorite.

In order to evaluate the mechanism of consumption of hydrogen peroxide on the surface and understand the role of the hydroxyl radical in the system, both the Ghormley and the Hantzsch spectrophotometric measurements were done. The results from the experiments are presented in the following paragraphs.

5.2 Experimental details

The copper oxides materials considered are in shape of powder, the characteristics of these powders are:

- copper (II) oxide powder (CuO) < 50 nm (CAS [1317-38-0])(99,99% ALDRICH)
- copper (I) oxide powder (Cu_2O) (CAS[1317-39-1]) (ALDRICH).

These two powders are in form of nanopowder, they are stored in an inert atmosphere for all the period in which experiments are performed in order to avoid the oxidative process due to exposition in the atmosphere. The shape of nanopowder makes very difficult the step of filtration of the solutions in which the powders are added.

The experiments performed involve both the Ghormley and Hantzsch analysis. The oxide powders are investigated in the same way as was previously described in the copper powder experiments, so that different amount of masses are inserted in a reactor vessel in which is present an aqueous solution. The solution is 100 ml of Millipore MilliQ water solution at a fixed concentration of 5mM of H_2O_2 at 100mM of CH_3OH, it is continuously purged with a constant flux of nitrogen in order to create an anoxic environment. The way used to prepare the aqueous solutions and the reactants used for the Ghormley and Hantzsch methods is the

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same already described in the previous chapters. The main difference in the oxide experiments compared to the ones performed with the copper powder concerns the filtration step. The solutions with oxide powders, as for copper powder, need to be filtered before being added in the probes in which are performed the Ghormley and Hantzsch methods. A sample from the reaction vessel is usually extracted with a syringe, this sample is then filtered and added in the probes with the corresponding reactant environment. The filtering of the solution containing nanopowder is not good enough to avoid particle dispersed; this inefficiency was proved with the analysis at ICP of these filtered solutions (chapter 3), they reveal an amount of particle dispersed of the order of few ppm. This such small amount of particles dispersed in the solution of the cuvette does not interfere with the spectrophotometric analysis. The few particles in solution indeed do not provoke the scattering of the light.

The filtering with the 0.2 μm filter is fine enough to allow the spectrophotometric analysis but does not allow the ICP analysis of the experimental solutions, as it was previously explained in chapter 3. Due to the impossibility of making valid ICP analysis of dissolved oxides in the aqueous solutions due to oxidative processes, the ICP analysis is not reported.

The way of making the experiment with the cuprite and tenorite follows exactly the same procedure used in the copper powder experiments.

5.3 Results

The investigation of the kinetics of consumption of hydrogen peroxide and production of hydroxyl radical is investigated at room temperature in two systems each containing the copper (I) oxide and the copper (II) oxide powder.

The different suspensions studied consider a different range in mass for the two powders. The experiments with cuprite cover a mass range between $0.1 - 5$ grams while the tenorite, that has a much smaller particle size, was investigated in a range of $0.01 - 0.15$ grams. This choice was done first in order to perform experiments with a similar surface to volume ratio, furthermore it depends on the speed rate of the reaction. If the reaction happens in a too fast way it is not physically possible to take enough samples useful in describing the kinetics of the reaction.

The aqueous solution used in these experiments has the same characteristics of that one used in the copper powder experiments, it means that the concentration of radical scavenger inserted is fixed at 100 mM. As it can be seen from figure 5.1b), the reaction vessel of each experiment is covered with a parafilm sheet in order to ensure an anoxic environment and avoid the leakage of solutions.

The mixing of the solution is performed with a magnetic stirrer that is set to a speed rate of 750 1/min. The results of the experiments are presented in two sections considering the two different materials involved, the experimental procedure is the same.

Figure 5.1 A picture of the aqueous cuprite system at the end of an experiment on the left 5.1a), a tenorite experiment ongoing on the right side 5.1b)

5.3.1 Cuprite

The cuprite experiments involve many different tests with the powder dispersed and stirred in the reaction solution. The cuprite is the most important oxide formed in the process of oxidation of copper, so that it was investigated in a wide range of masses in order to have many results of kinetics. The results achieved are presented below and the discussion is given in the last paragraph of this section.
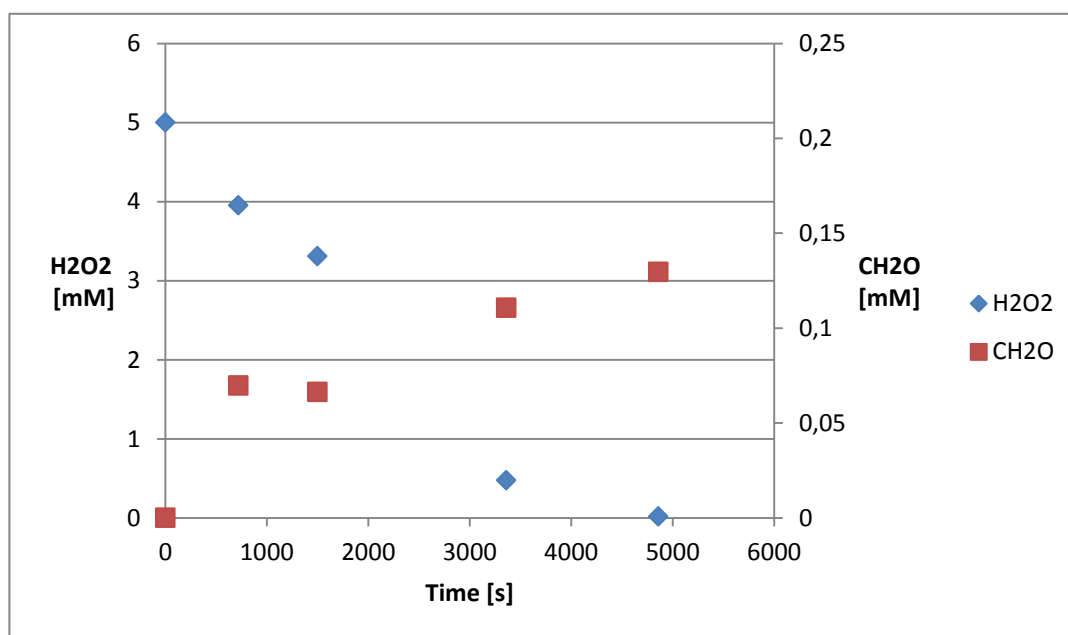
Figure 5.2 Cuprite powder 0.1 gr (28 August) , CH_3OH 100mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time
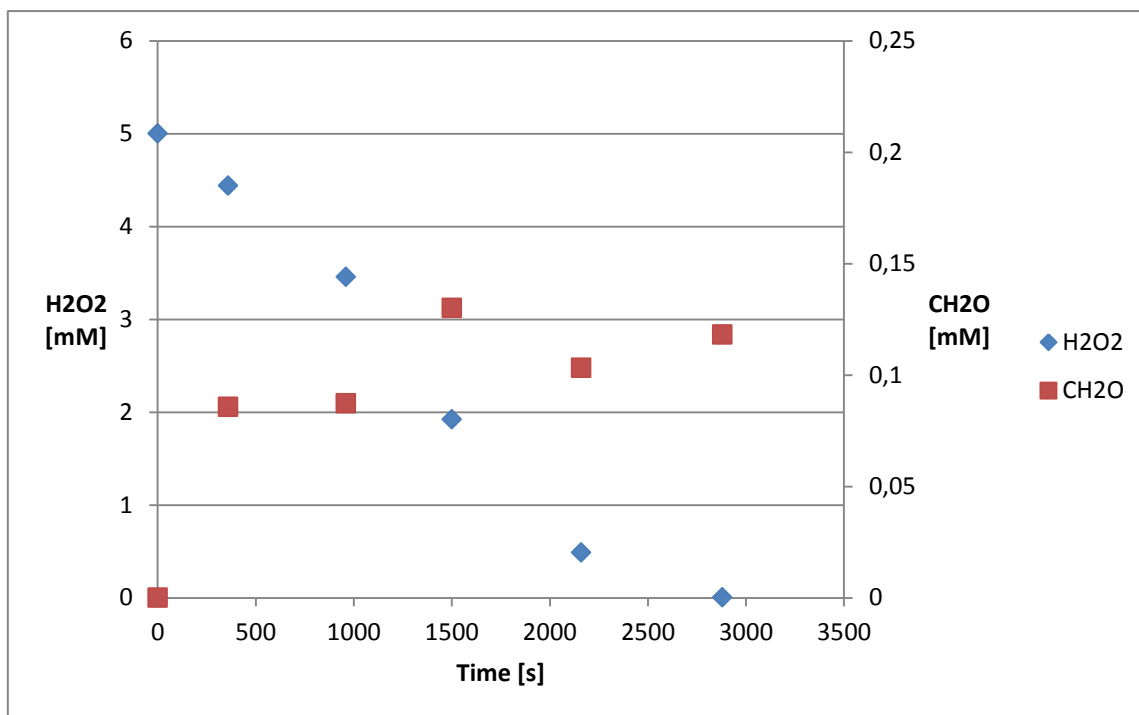
Figure 5.3 Cuprite powder 0.5 gr (27 August) , CH₃OH 100mM , H₂O₂ 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time
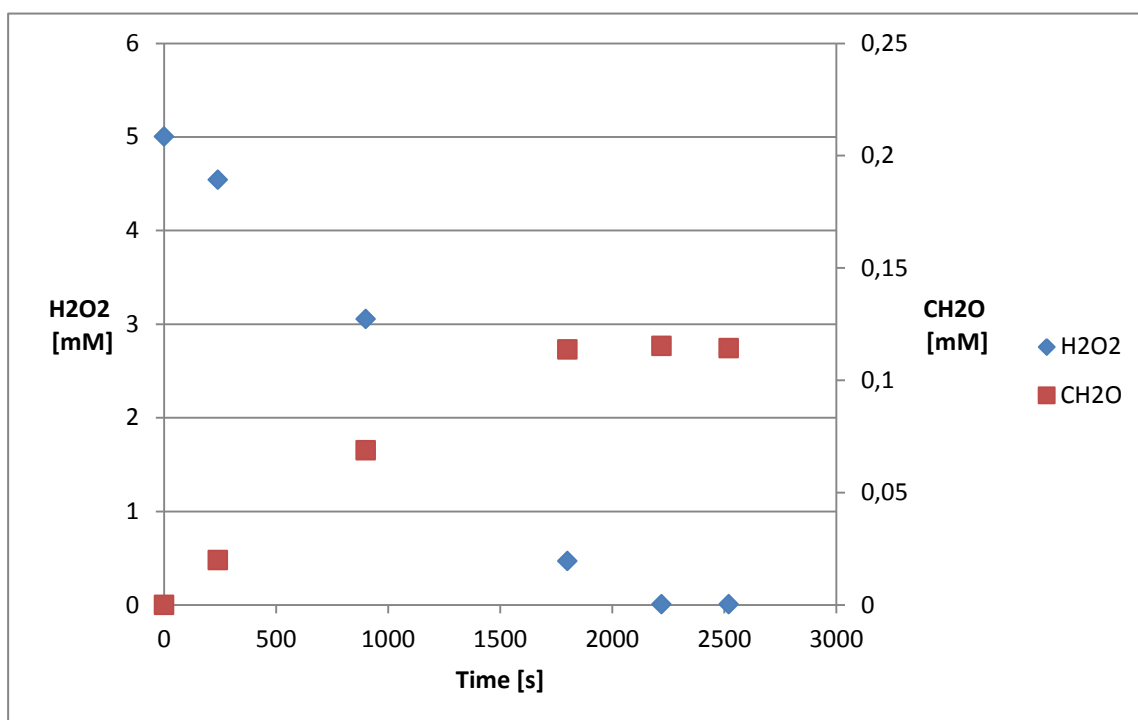

Figure 5.4 Cuprite powder 0.75 gr (26 August) , CH₃OH 100mM , H₂O₂ 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time
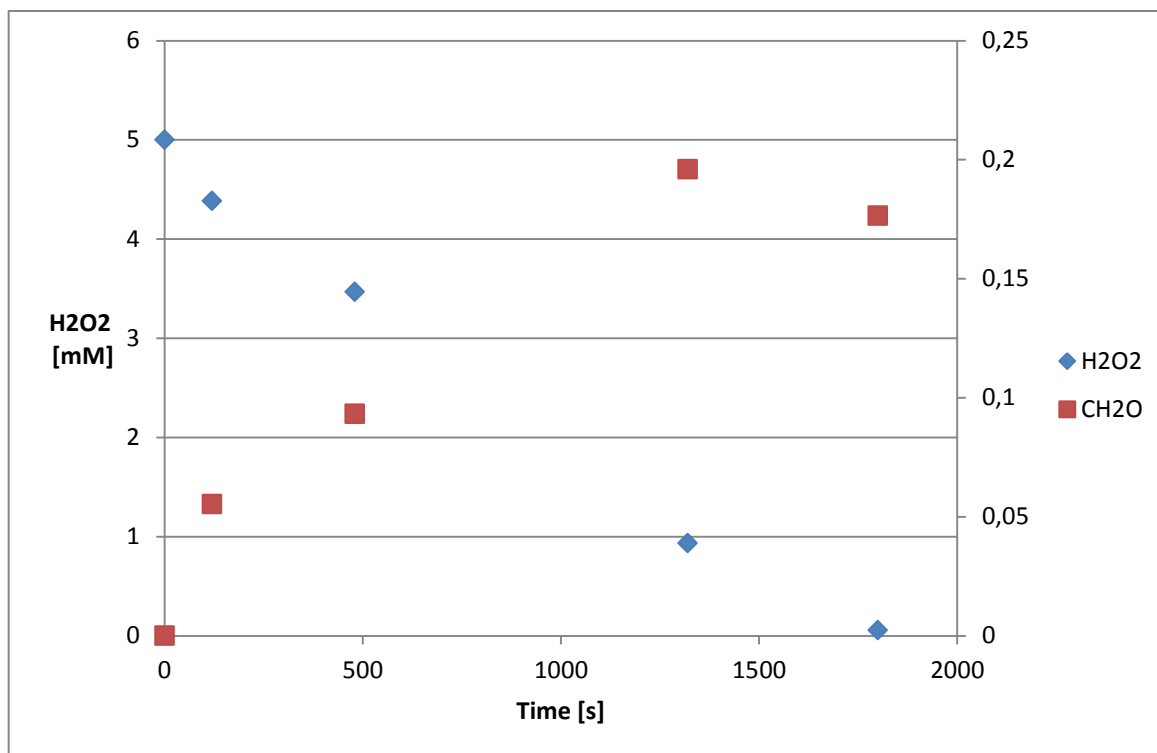
Figure 5.5 Cuprite powder 1.25 gr (27 August) , CH₃OH 100mM , H₂O₂ 5mM : evolution in the concentrations of H₂O₂ and CH₂O as a function of reaction time
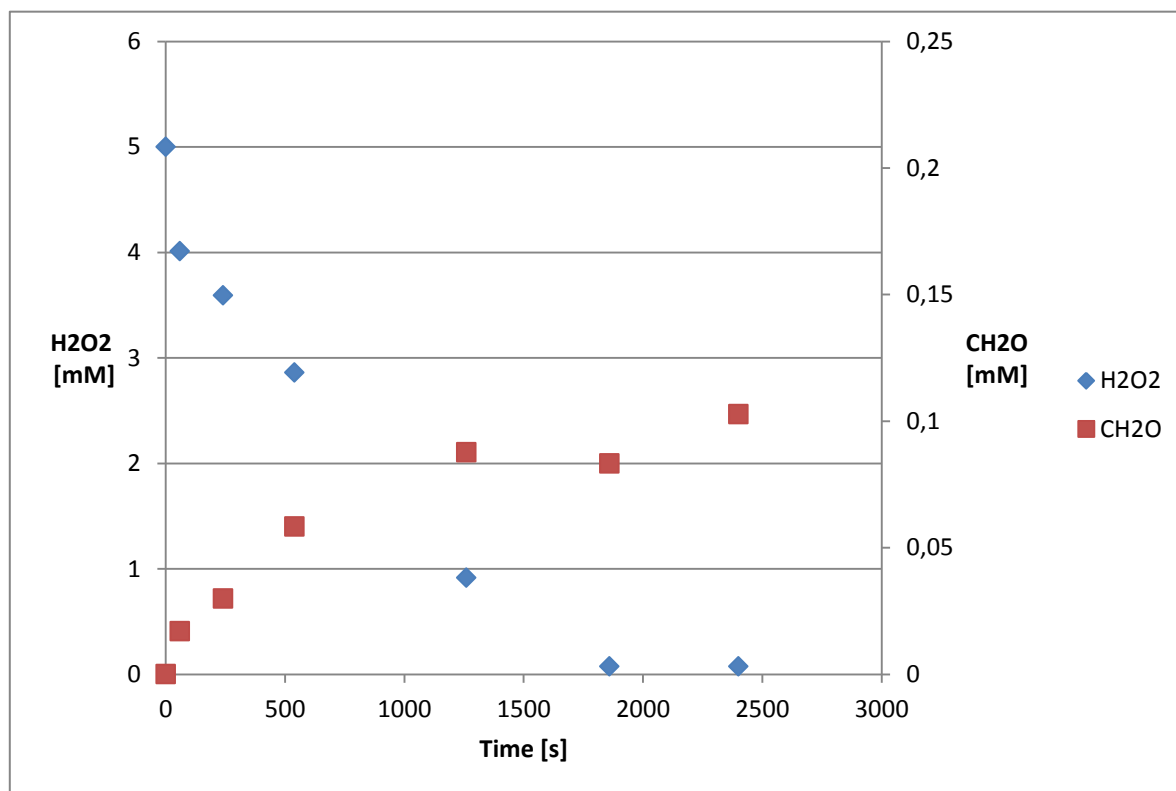

Figure 5.6 Cuprite powder 2 gr (29 August) , CH₃OH 100mM , H₂O₂ 5mM : evolution in the concentrations of H₂O₂ and CH₂O as a function of reaction time
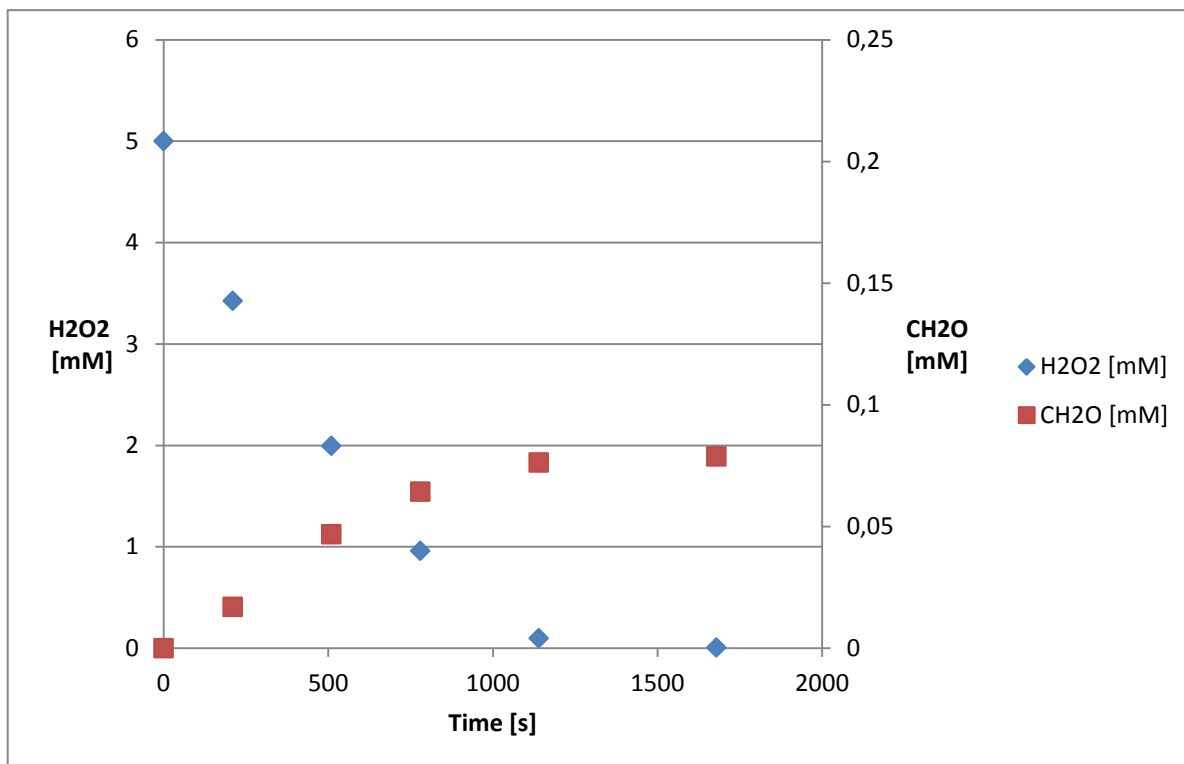
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Figure 5.7 Cuprite powder 5 gr (9 September) , CH_3OH 100mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time

5.3.2 Tenorite

The tenorite experiments cover a much smaller range of masses compared to the previous cuprite tests. The copper (II) oxide nanopowder consists of really small particles with a diameter size of about 50 nm. The surface area to volume ratio for this compound is really much higher if comparing samples of same weight of copper powder or cuprite powder. In fact these two last materials have an average particle diameter that is about three times larger than the CuO powder, so that the mass involved in the experiments is much smaller. Estimating the total surface area of the different oxide powders involved in each experiment as the surface area of as many spheres as many particles are related to the mass inserted, it is demonstrated that the tenorite has a surface area about ten times larger than the copper and cuprite powders, for this reason is needed only a smaller amount of mass in the system.

The first experiment performed, figure 5.12, involves a really small amount of tenorite powder if compared to the masses used in the copper powder experiments, but as previously said is not possible to compare these materials regarding their weight. Even if it would be interesting to test even much larger amount of powder, the fast reactivity of the copper (II) oxide does not allow the sampling of the solution.

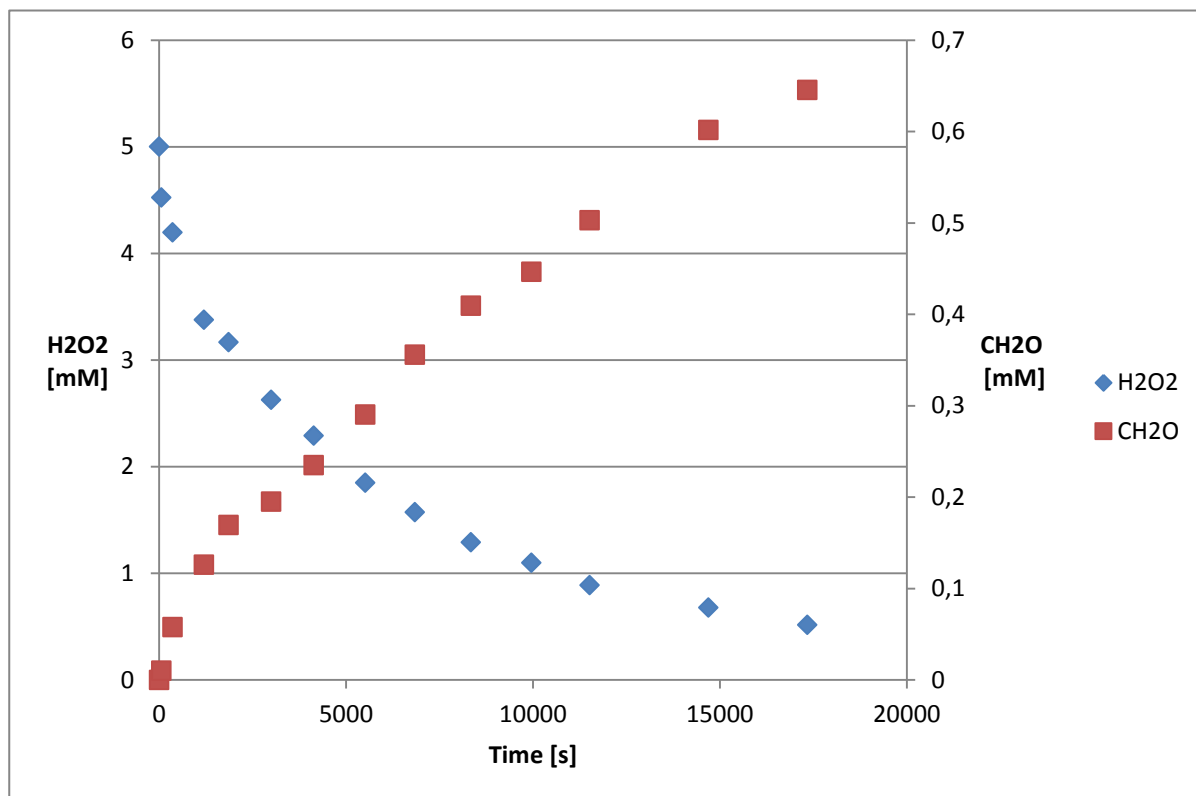The results of the experiment performed are presented below.

Figure 5.8 Tenorite powder 0.01 gr (16 July) , CH_3OH 100mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time
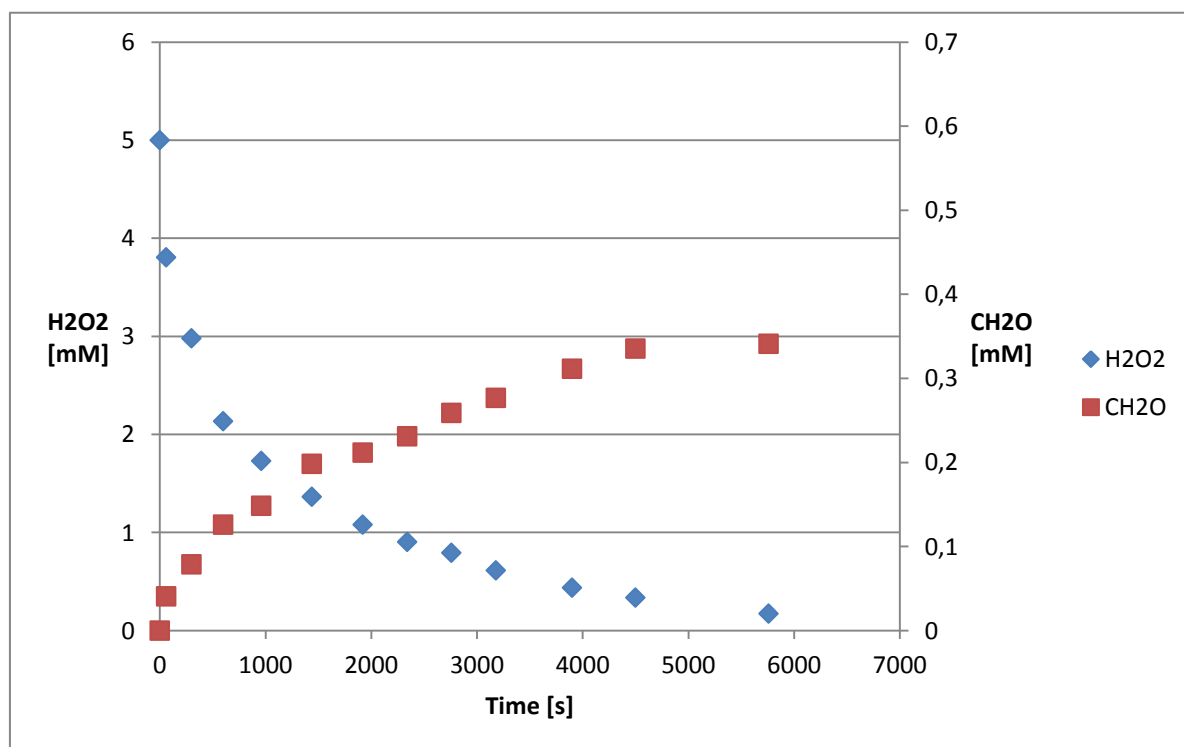
Figure 5.9 Tenorite powder 0.025 gr (15 July) , CH_3OH 100mM , H_2O_2 5mM : evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction tim

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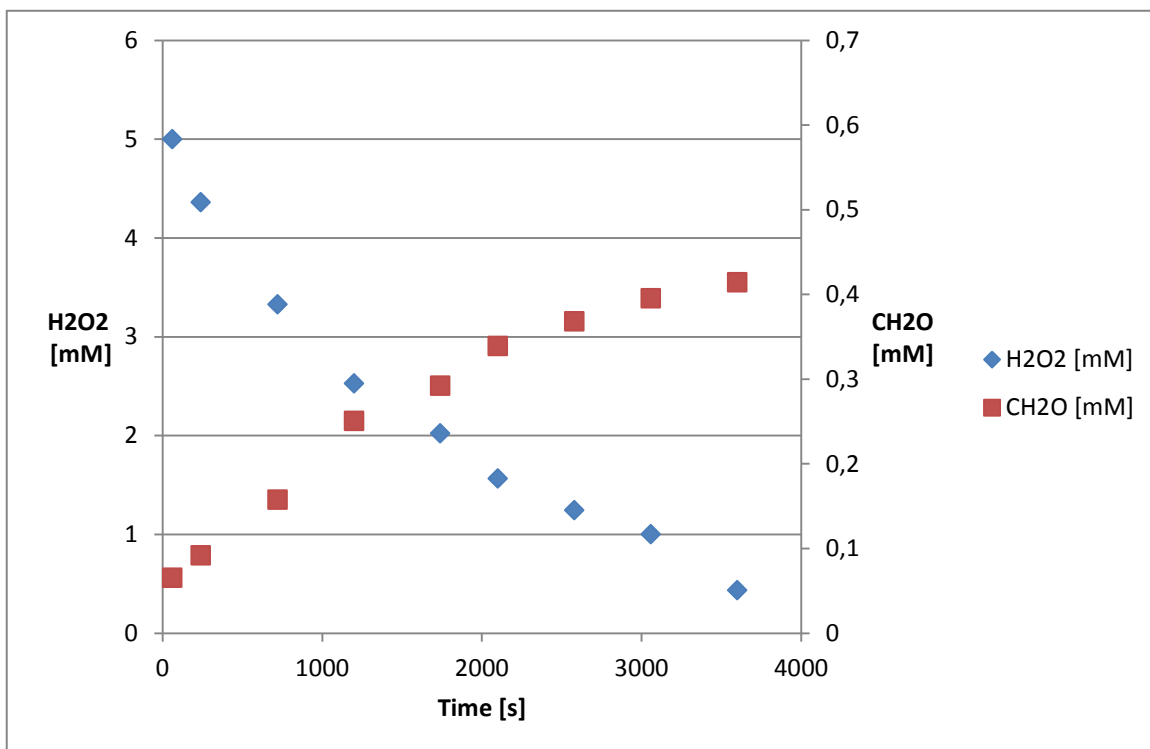
Figure 5.10 Tenorite powder 0.05 gr (8 July) , CH$_3$OH 100mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time
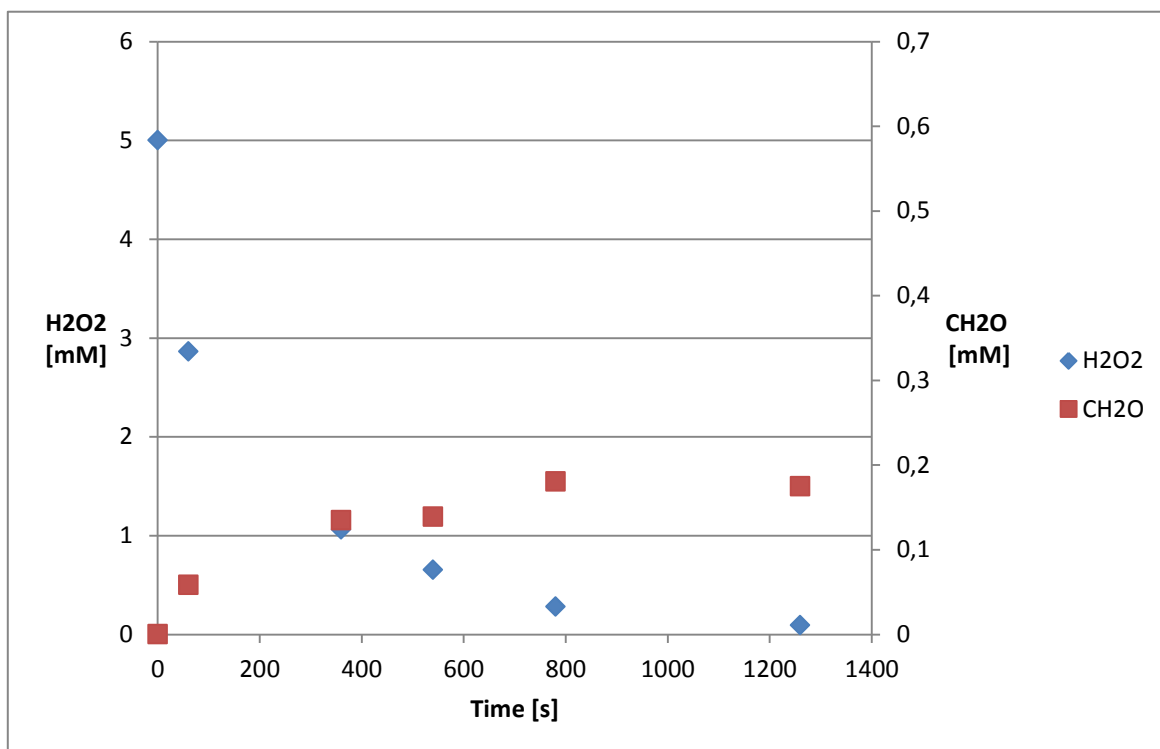
Figure 5.11 Tenorite powder 0.075 gr (15 July) , CH$_3$OH 100mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time
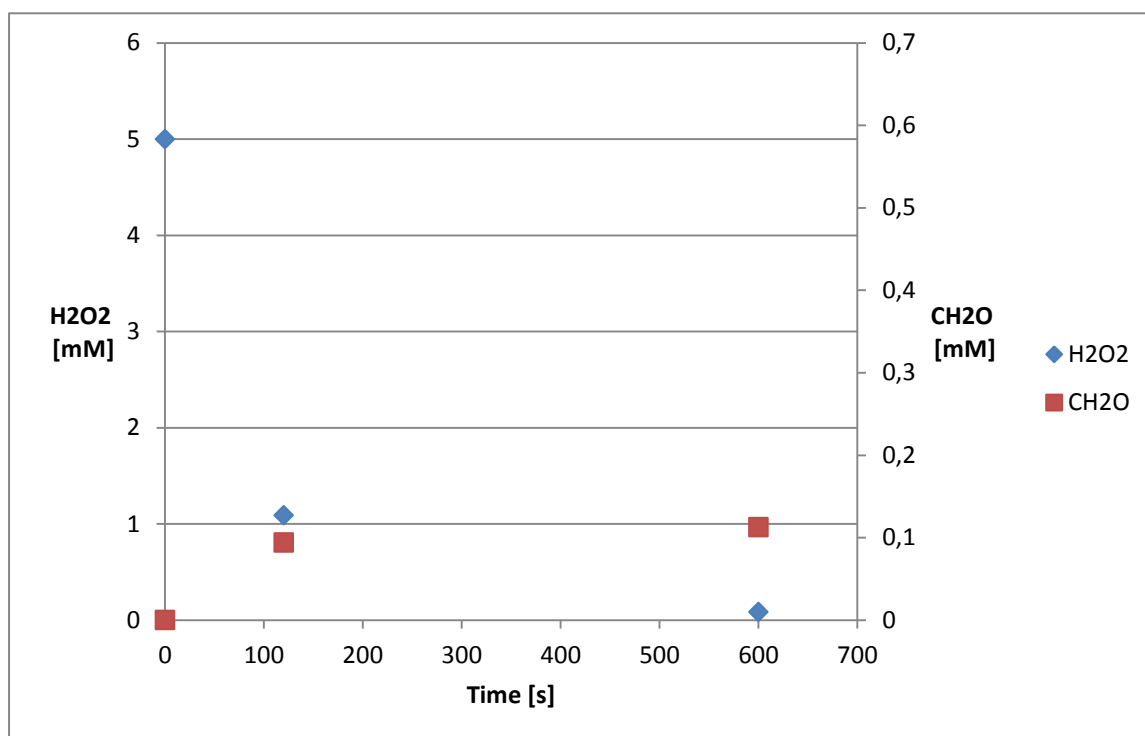
Figure 5.12 Tenorite powder 0.15 gr (8 July) , CH$_3$OH 100mM , H$_2$O$_2$ 5mM : evolution in the concentrations of H$_2$O$_2$ and CH$_2$O as a function of reaction time

5.4 Discussion of results

The behavior of the two oxides is really different. From the experiments performed is evident that for both the powders, the reactivity of the system increases at higher quantities of mass involved in the reaction vessel. This behavior makes sense considering the fact that at higher quantities of powder the surface to volume ratio increases and so the reactivity of the system increases. It is in fact much easier for a molecule of hydrogen peroxide to reach the surface of the copper oxide powder if more particles are circulating in solution.

The processes that involve the surface of powder in contact with the hydrogen peroxide solution are basically two : a first adsorption of H$_2$O$_2$ on surface and the decomposition of the adsorbed H$_2$O$_2$. The initial faster disappearance of hydrogen peroxide in solution, evident in the cuprite experiments, is due to the rapid process of adsorption.

The very much different behavior among the two oxides is about the kinetics of formation of formaldehyde. The concentration of H$_2$O$_2$ added in the reaction solution is in every experiment exactly a fixed amount, but the detection of formaldehyde in the system is really different.

The comparison between all the data involving the copper (I) and (II) oxides is possible because it was used the same experimental conditions, procedures and methods.

A descriptionn of the kinetics of consumption of hydrogen peroxide and formation of formaldehyde for the two oxides follows below.
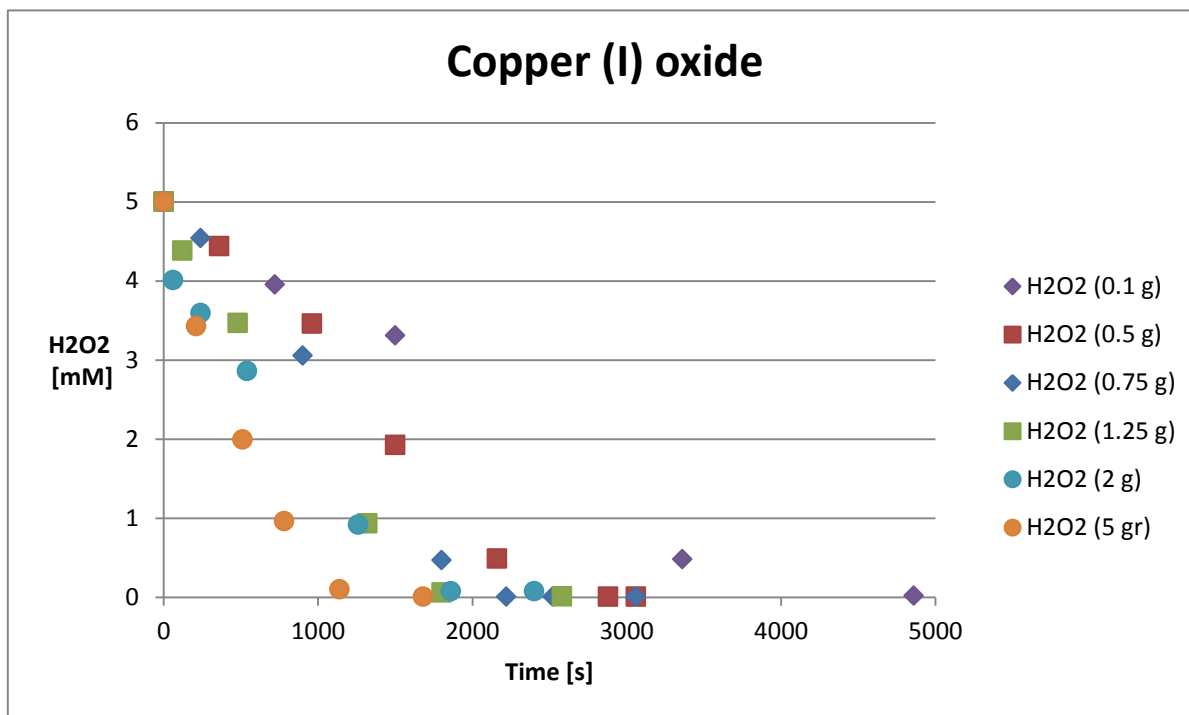
Figure 5.13 Amount of hydrogen peroxide present in the reaction system as a function of reaction time in cuprite experiments at different mass amount
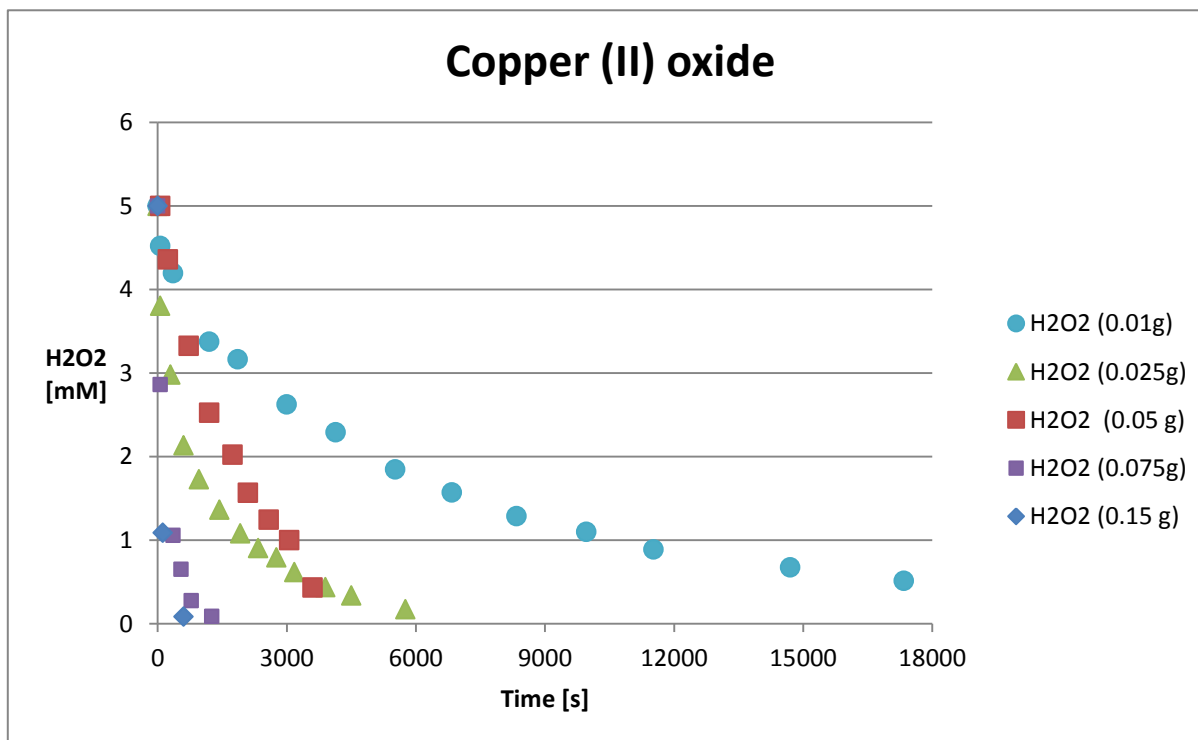
Figure 5.14 Amount of hydrogen peroxide present in the reaction system as a function of reaction time in tenorite experiments at different mass amount

Figure 5.15 Formaldehyde formed by reaction of HO radicals with methanol during decomposition of H_2O_2 (5mM, 100 ml) catalyzed on cuprite experiments at different mass amount

Figure 5.16 Formaldehyde formed by reaction of HO radicals with methanol during decomposition of H_2O_2 (5mM, 100 ml) catalyzed on tenorite experiments at different mass amount

From the plots (figures 5.13, 5.14) is evident that increasing the surface area in both cuprite and tenorite experiments, the reactivity towards H_2O_2 increases, so that the total consumption of hydrogen peroxide is faster. This is due to the fact that reducing the surface area the capacity for the powders to adsorb hydrogen peroxide on the surface decreases.
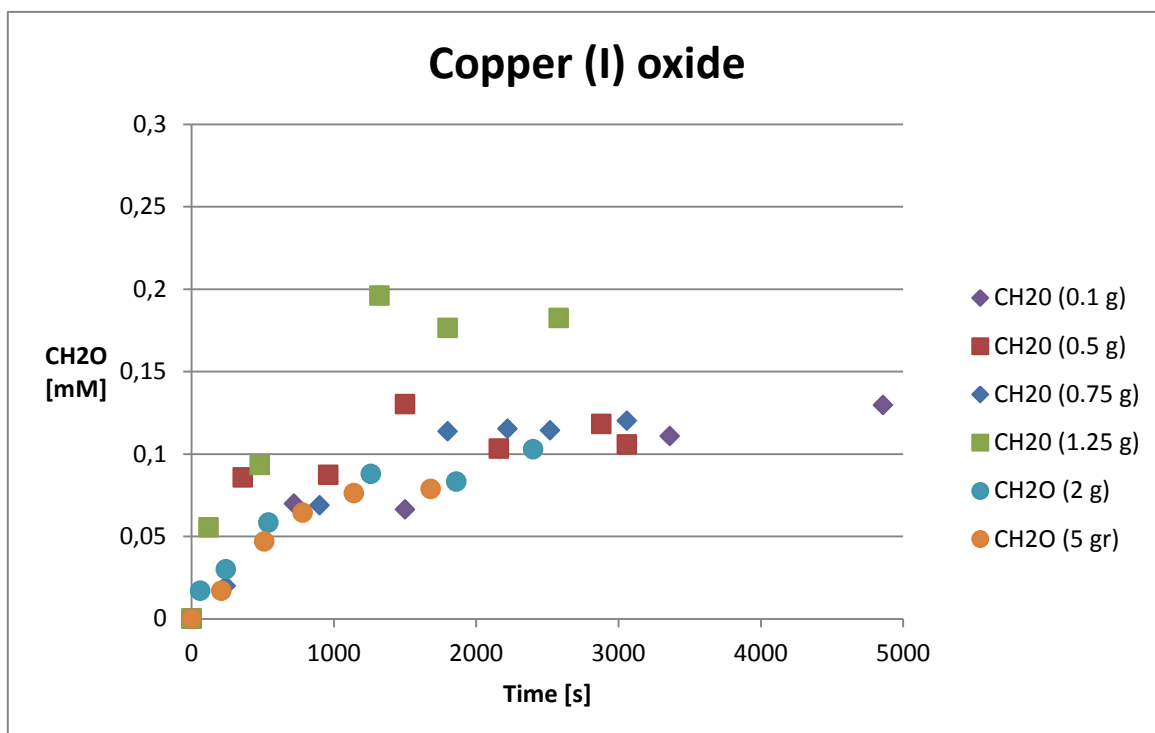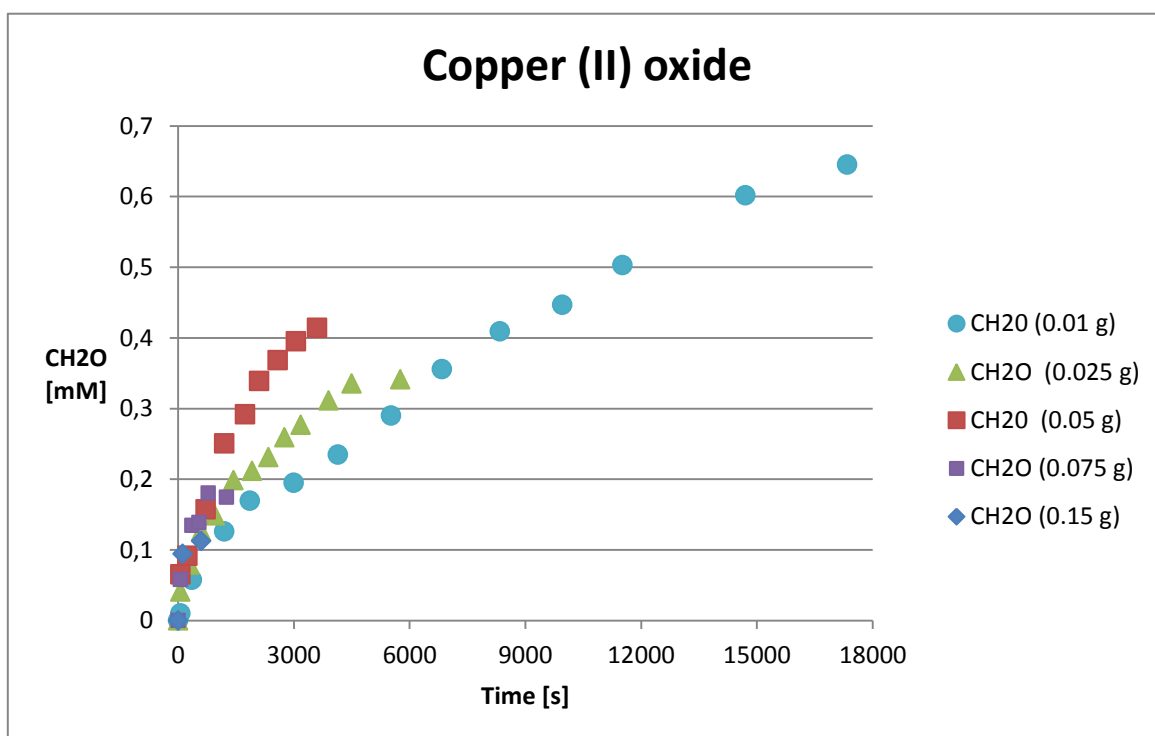
Regarding the amount of CH_2O produced in the system, it depends not only on the amount of hydrogen peroxide inserted in solution, that is the same in every experiment. The formation of formaldehyde mainly depends on two factors: the amount of hydroxyl radicals formed in the decomposition of H_2O_2 and their relative reactivity in the system.

Furthermore the dynamics of the formaldehyde releases from the oxide surface might be related to the specificity of the oxide surface.

The large releases of formaldehyde detected by spectrophotometric analysis in tenorite experiments might be related to the kinetics and the processes involved in the surface of this material. In the proposed mechanism of decomposition of H_2O_2 (1) few pathways regarding the production of hydroxyl radicals are possible, in a system in which the catalytic decomposition is a fast process compared to the adsorption one, large amounts of $HO\cdot$ are expected to be formed.

An analysis in deep of the processes involved on the surface of the oxides in contact with hydrogen peroxide is presented in chapter 7 where all the results achieved in this work are compared and analyzed.

Chapter 6

KBS-3 Copper canister analysis: kinetics of copper surface reactions

In this chapter the results obtained in the analysis of corrosion resistance properties of the pure metallic copper used in KBS-3 canisters are presented. The experimental analysis considers several cubic copper canister samples that have been subject to hydrogen peroxide experiments in combination with irradiation experiments. The purpose of this analysis is the investigation of the consequences of H_2O_2 in contact with the copper canister surface in an anoxic aqueous environment.

6.1 Investigation of corrosion processes on copper surface

The evaluation of the kinetics of consumption of hydrogen peroxide and the trend of production of hydroxyl radicals in the copper oxides and copper powder experiments had the purpose of clarifying some mechanistic aspects involved in the radiation induced corrosion of copper. As previously stated the purpose of this work is to evaluate the stability of the pure copper canister surface in contact with an aqueous anoxic environment exposed to ionizing radiation. The assumption of stability and inertia of copper in this kind of environment was questioned with the previous experiments that show that there is a reactivity of the pure copper powder in contact with the products of water radiolysis.

In order to fulfill the analysis and give reliability of the results obtained, some copper cube samples cut directly from a SKB copper canister wall were used in an experimental series. The experimental plan includes the Ghormley method and Hantzsch method analysis, in order to investigate the kinetics of consumption of hydrogen peroxide and the formation of hydroxyl radical on the surface, and irradiation experiments.

The samples used for this experimental series had the same shape and size in order to achieve an overall view for the behavior of copper in contact with hydrogen peroxide, many conditions were experimented.

The radiation induced corrosion is a complex phenomenon that is not easy to represent and investigate through laboratory conditions. The products of the water radiolysis, produced by the irradiation of water in contact with the copper canisters containing the spent nuclear fuel, are simulated by solutions containing a certain amount of hydrogen peroxide. As already said the most important oxidant species among water radiolysis products is the H_2O_2.

The concentrations of hydrogen peroxide used in reaction solutions are higher than the real hypothetical values that would be produced when the water enters in contact with the copper canisters. The long time frame during which the canisters would be exposed to an aqueous environment makes difficult to perform realistic experiments. The irradiation experiments and the hydrogen peroxide ones, simulate a much more aggressive environment than the real one but it is the fastest and easiest way to analyze and understand which are the most important processes that will affect the stability of the copper canister.

The experimental plan has the purpose to discover the reactions involved and then make a long term prediction on the basis of the phenomenon evaluated in a short term period.

The assumption of stability of copper surface in contact with an aqueous anoxic environment is here questioned, the reactions to be investigated regard the reactivity of hydrogen peroxide on the surface of pure metallic copper and the role of its decomposition on the production of hydroxyl radicals. The HO· is another important oxidant species that can affect the corrosion resistance properties of copper.

6.2 Experimental details and results

In order to investigate the capability of copper canisters of KBS-3 to withstand the corrosion processes induced by irradiated water, experiments involving samples cut from a piece of the copper canister produced by SKB for the KBS-3 concept are used.

It is here remembered that the copper canister wall is made of pure copper (99.992 % Cu, with major impurities of Ag and P, respectively 25 and 30-70 ppm maximum), from this piece many samples were cut. The shape of the samples is cubic with dimensions of $10\times10\times10$ mm^3, before each experiment the samples were polished with a SiC abrasive paper of 800 grit. After the polishing of all the faces, one face was further polished with a 3 μm polycrystalline diamond paste add on the paper, the polishing was made in 99.5 % ethanol. After this step the samples were placed in a solution of 95 % ethanol in an ultra-sonic bath for few minutes in order to clean the surfaces from all the contaminants produced during the process of cutting.

The samples were then dried with pure nitrogen and stored in a glovebox before the experiment.

Two types of experiments were performed with the copper cubes, the irradiation experiments in the gamma source and the hydrogen peroxide experiments.

Some experiments performed with the gamma source in previous papers [16] are here compared with the ones performed for this work.

The experimental series with the copper cubes was basically carried out with the Modified Hantzsch and Ghormley methods. The samples were placed in solutions containing different amounts of hydrogen peroxide at a methanol concentration of 100mM, that is the same

scavenger concentration used in all the experiments performed with copper and copper oxides powders.

The reason of using different quantities of hydrogen peroxide is due to the fact that all the samples used have the same size, and thereby the same surface area, so it is impossible to vary the surface area in order to compare the kinetics of the reaction. The effects of corrosion are not compared on the basis of surface area but on the basis of hydrogen peroxide concentration.

The solutions used in the experiments are the same already described in previous chapters, all the methanol, hydrogen peroxide solutions were prepared with water from Millipore MilliQ system. All the solutions used in the experiments were first purged for approximately 30 minutes in order to simulate an anoxic aqueous environment.

The cube sample is placed in the reaction vessel with the finest polished surface on the top, at the end of each experiment a sample from the reaction solution is taken out and analyzed with the ICP-AES (Inductively coupled plasma atomic emission spectroscopy). The ICP analysis allows the quantification of copper releases in solution due to corrosion processes of the surface. The estimation of the releases of copper in solution points out the role of hydrogen peroxide in the corrosion reactions involving the surface of copper.

In order to understand which signs of corrosion are produced on the surface due to the action of the hydrogen peroxide, the samples were analyzed with a Jeol JSM-6490LV scanning electron microscope, SEM. This instrument allows the estimation and characterization of the oxide layer formed on the polished surface.

To better correlate the corrosion signs due to the exposure of copper cubes to hydrogen peroxide solutions with the action of hydrogen peroxide formed during the radiolysis of water, some irradiated cubes were analyzed with SEM. The images of the surfaces exposed to hydrogen peroxide and exposed to irradiation are then compared. The discussion of these results is given in the following sections.

6.2.1. Hydrogen Peroxide experiments

In chapter 3 two experiments involving copper cube samples placed in a solution 0.5mM of H_2O_2 were presented. The consumption of hydrogen peroxide in contact with copper cubes is a slow process compared to the copper powder experiments. In copper powder experiments the total consumption of hydrogen peroxide is reached between one and two hours, due to the powder amount used. The copper cube experiments need a much longer time for the total consumption of the hydrogen peroxide.

After some calculations it was possible to estimate the approximate surface area ratio between the copper powder and copper cube experiments.

It is assumed that the copper powder is made by spherical particles with a diameter of 0.0965 mm, indeed the copper powder has a MESH -100 +325 that means that the particles have a diameter within the range of 0.044 mm – 0.149 mm. The calculations on surface area for a certain amount of powder ended up with the result that the surface area of 1 gram of copper powder is approximately 12 times larger than the surface area of a copper cube sample. This is probably the cause of the longer period of time needed for the copper cube experiment, at same conditions of the copper powder experiments.

In order to follow the kinetics of consumption of hydrogen peroxide and its role in the production of formaldehyde, an overnight experiment was planned. From the experiments at 0.5mM previously performed, it was supposed that the experiments at 5mM of H_2O_2 lasts around 20 hours.

The overnight experiment considers two experiments performed at the same time, in order to investigate the role of hydrogen peroxide as main oxidant species able to corrode and affect the copper surface, two cubes were exposed in a solution 100ml at 5mM of H_2O_2, 100mM CH_3OH. One cube sample is a polished cube, the second cube inserted in the other reaction vessel at same conditions and with the same purged solution is a polished cube that was previously stored in a reaction vessel containing a purged solution of hydrogen peroxide 2.5mM for 48 hours. The storage of the cube for two days allowed the total consumption of hydrogen peroxide, the polished cube after this period is called from now "preoxidized" because it was exposed to an oxidant environment before being used in the hydrogen peroxide experiment. A representation of the overnight experiment follows below.
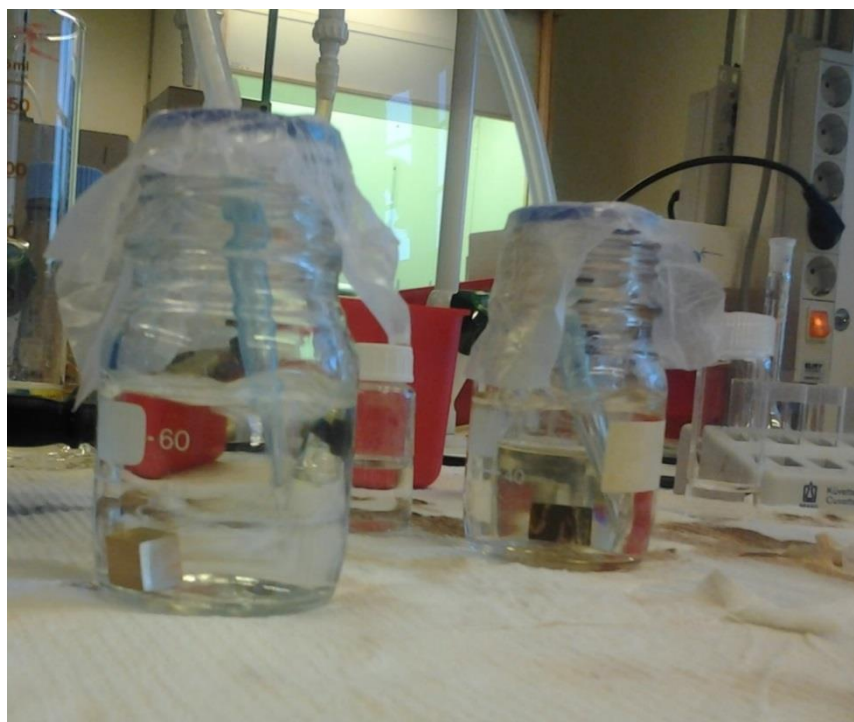

Figure 6.1 Depiction of the overnight experiment: two polished cubes are exposed at a solution 100ml with composition of 100mM CH_3OH 5mM H_2O_2. The reaction vessel on the right contains the preoxidized cube.

The two reaction vessels are identical and are purged through the same nitrogen flow rate, the preoxidized cube at the beginning of the experiment did not show any corrosion features while during the experiment, as it can be seen in figure 6.1, some black spots covered all the surface.

In the figure 6.2 the preoxidized cube, on the right side, has evident black spots all over the surfaces: the surface appears much more corroded compared to the polished cube. At the end of the experiment both the cubes are dried and then analyzed with the SEM in order to characterize the corrosion features.

In the copper cube experiments the stirring of solution is made by the purging action of the nitrogen flow.

At the end of the experiment the two cubes had a remarkable difference in the appearance: the preoxidized cube had many dark spots all over the surfaces while the polished cube after being exposed to an oxidant environment did not seem visibly corroded.

A representation of the copper cube samples at the end of the experiment is presented below.

Figure 6.2 Depiction of the copper cube samples used in the overnight experiment, polished cube on the left and preoxidized cube on the right side.

The analysis carried with the Modified Hantzsch method and Ghormley method were performed with the same reactant solutions for both the experiments in order to guarantee the same experimental conditions.

The sampling of the two experiments was performed at the same time with only few minutes of difference between the sampling of each reaction vessel. The kinetics of reaction of the two experiments was followed at the same way. The results from the sampling of the solutions are presented below, every hour a sample for each reaction vessel was taken and both the Modified Hantzsch method and the Ghormley method analysis were performed.
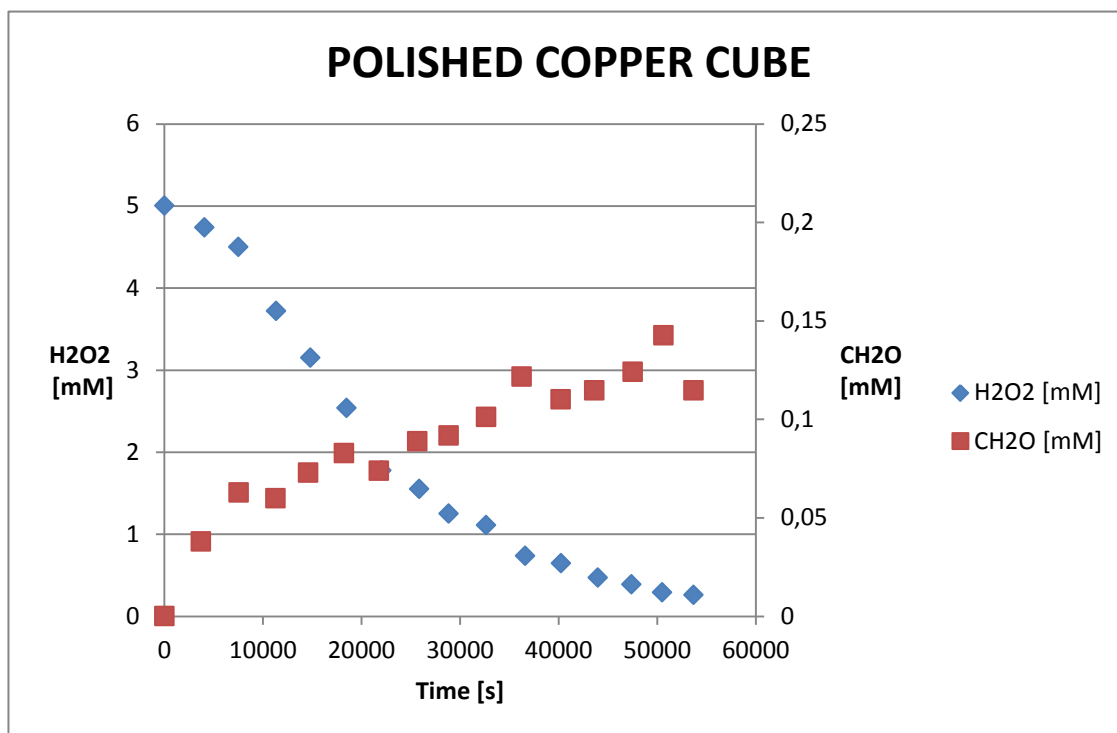
Figure 6.3 Evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time, polished copper cube exposed to 100ml solution at 100mM CH_3OH, 5mM H_2O_2.
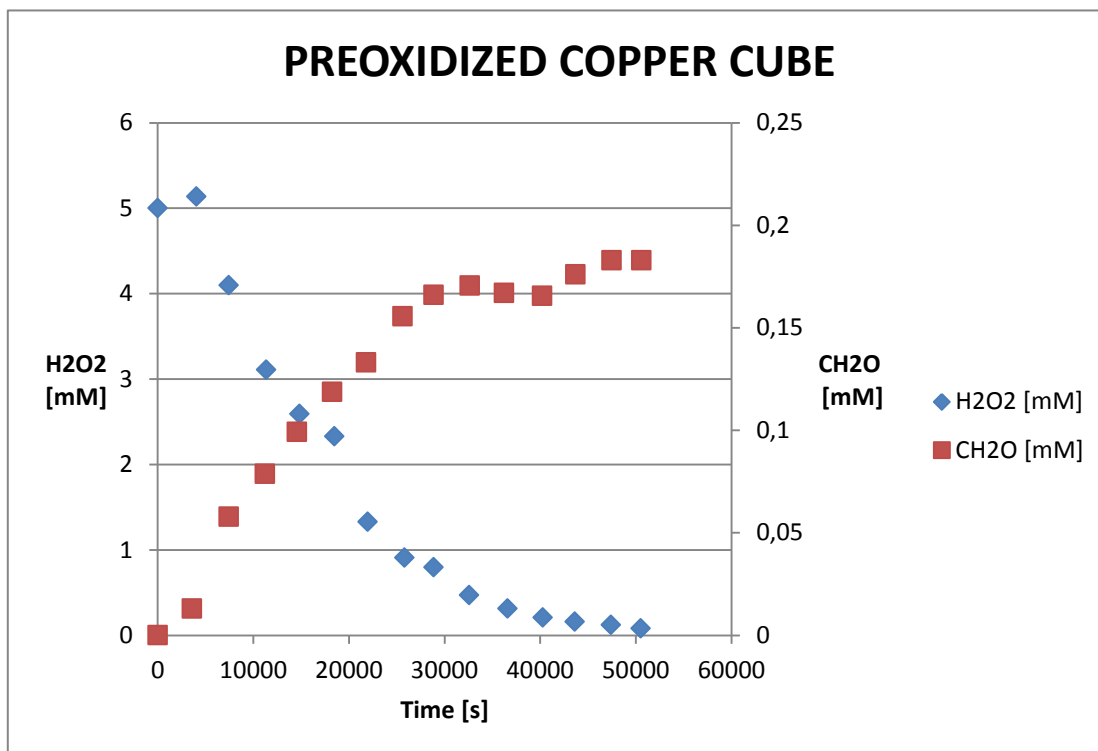

Figure 6.4 Evolution in the concentrations of H_2O_2 and CH_2O as a function of reaction time, preoxidized copper cube exposed to 100ml solution at 100mM CH_3OH, 5mM H_2O_2.

The corrosion processes from an observable point of view seem considerably different between the two cubes, but the kinetics of consumption of hydrogen peroxide and formation of formaldehyde showed in figure 6.3 and 6.4 are quite similar.

The preoxidized cube shows a much steep trend of consumption of hydrogen peroxide, especially at the beginning in the first hours but from a global point of view the total consumption of H_2O_2 happens almost at the same period of time of the polished cube.

The formation of formaldehyde in the preoxidized cube experiment reaches slightly higher values of concentrations compared to the polished cube one.

Thanks to this overnight experiment it was possible to evaluate the overall kinetics of formation of CH_2O and consumption of H_2O_2.

In the next experiments involving copper cube samples the kinetics is not followed continuously, for obvious reasons, but the concentration of formaldehyde at total consumption of H_2O_2 and the trend of consumption of hydrogen peroxide are investigated. In this case the concentration of hydrogen peroxide in solution is 3mM, this allows a characterization of the influence of the concentration of hydrogen peroxide in the formation of formaldehyde and on the corrosion processes on the surface.

The purpose of next experiments is not the evaluation of the overall kinetics, that was already investigated through the overnight experiment, but the corrosion features due to the presence of hydrogen peroxide. The corrosion features are investigated with ICP analysis of the solutions and the SEM analysis of the surfaces.

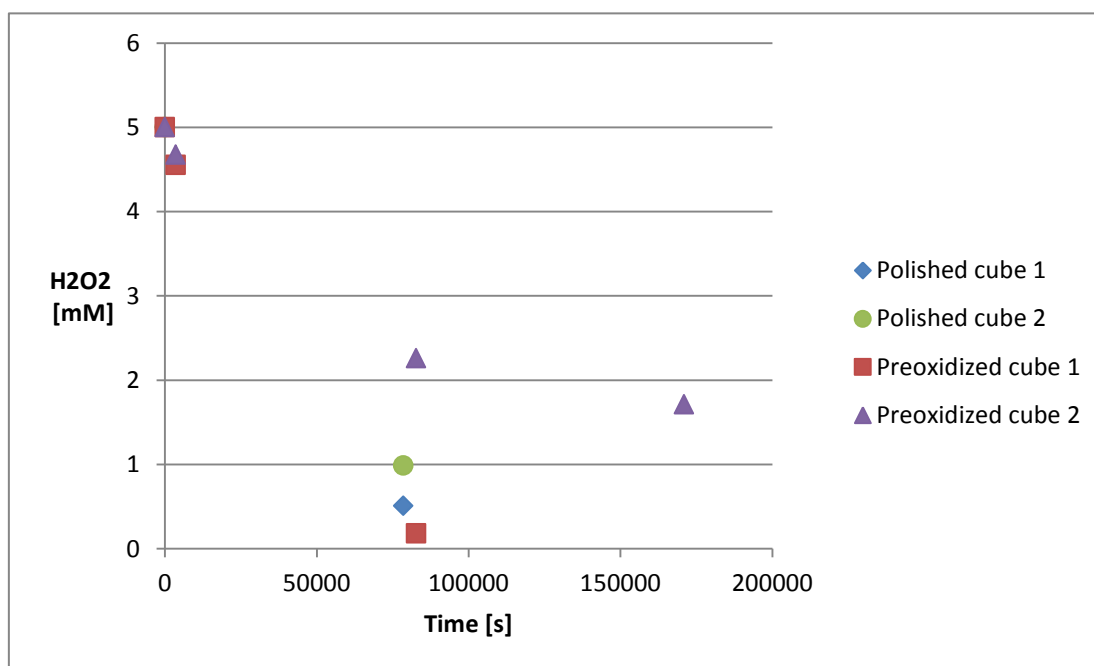In the next graphs the results obtained in experiments with other copper cube samples are shown.

Figure 6.5 Evolution in the concentrations of H_2O_2 during the reaction of copper cube samples polished and preoxidized in contact with a solution 100mM CH_3OH and 3mM H_2O_2.
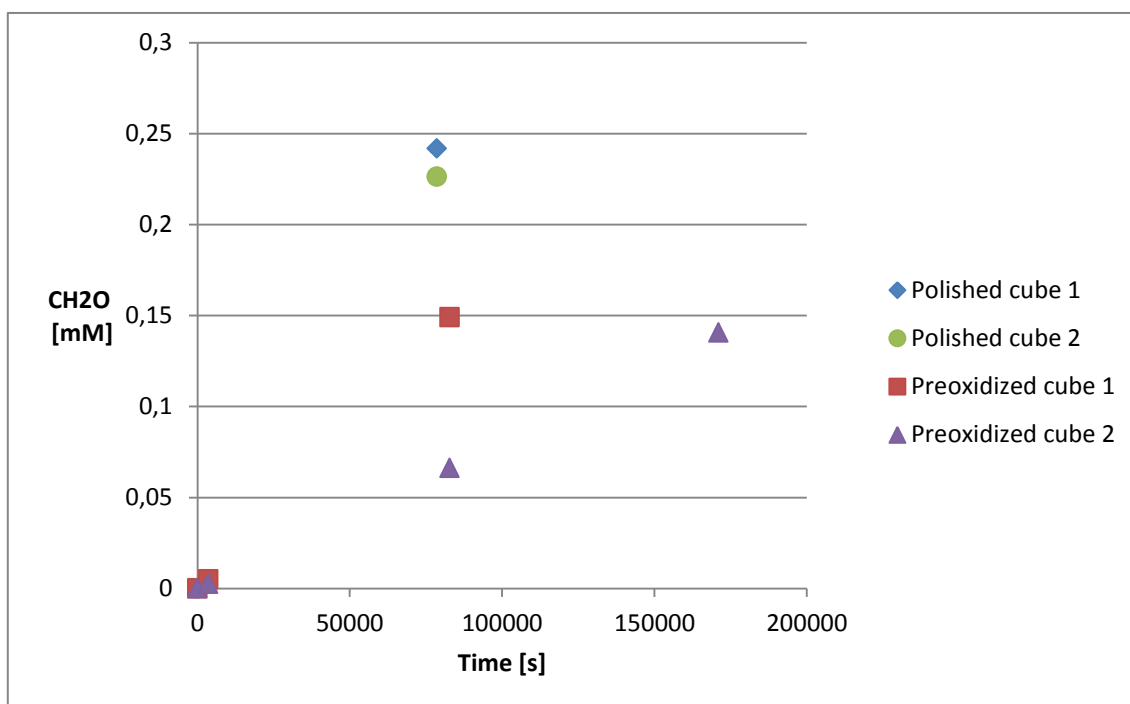
Figure 6.6 Evolution in the concentrations of CH_2O during the reaction of copper cube samples polished and preoxidized in contact with a solution 100mM CH_3OH and 3mM H_2O_2.

The graphs 6.5 and 6.6 show the behavior of two copper cube samples, the experiments were performed with two reaction vessels that run simultaneously. Each copper cube sample was polished and was inserted in each reaction solution, the results obtained from the run of these samples are named polished cube 1 and 2

After this experiment the cubes were dried and another experiment run at same conditions, the polished cubes during the first experiment were exposed to an oxidant environment, they were named after that preoxidized cube 1 and 2. These two samples were then inserted in the new reaction solution and the second experiment was performed.

The results obtained with these experiments reveal an important and unexpected behavior: the preoxidized copper cube 2 during the second experiment was somehow inert towards the hydrogen peroxide environment. After more than two days of experiment the consumption of hydrogen peroxide was stable at a certain value. It seems that the preoxidation layer carried by the hydrogen peroxide in contact with the polished cube in the first experiment had formed a homogeneous oxide layer that kept the copper surface safe from further corrosion processes or attacks. This behavior is even seen visibly : the copper cube 1 after the first experiment displayed the black spots all over the surface as recorded in figure 6.2, the oxidative process was visible. The copper cube 2 that was exposed to the same procedure of cube 1 after the first experiment had the same features of the figure 6.2 for the polished cube.

The copper cube 1 after the second run was visibly much more corroded than at the end of the first experiment, while the copper cube 2 did not present any corrosive features after the first experiment and it displayed the same appearance even at the end of the second run.

The corrosion features showed in figure 6.2 in this case represents the behavior of the surface in contact with the oxidant environment. But this behavior is not representative of every experiment, in order to better understand which damages the corrosion of hydrogen peroxide carried on the surface of the copper cubes a SEM analysis was made.

6.2.2 SEM analysis

The analysis and characterization of the surfaces of copper cube samples was carried out with the SEM –EDS instrument. After each experiment involving a copper cube sample, the cube was dried with nitrogen, stored in a plastic bag filled with nitrogen and analyzed with the scanning electron microscope.

In order to compare the surfaces before and after each experiment, and evaluate the corrosion features due to the influence of hydrogen peroxide a reference sample was analyzed. The reference sample is a polished copper cube that was stored in an inert atmosphere before the analysis. A representation of the surface of the reference sample is in the figure 6.7.
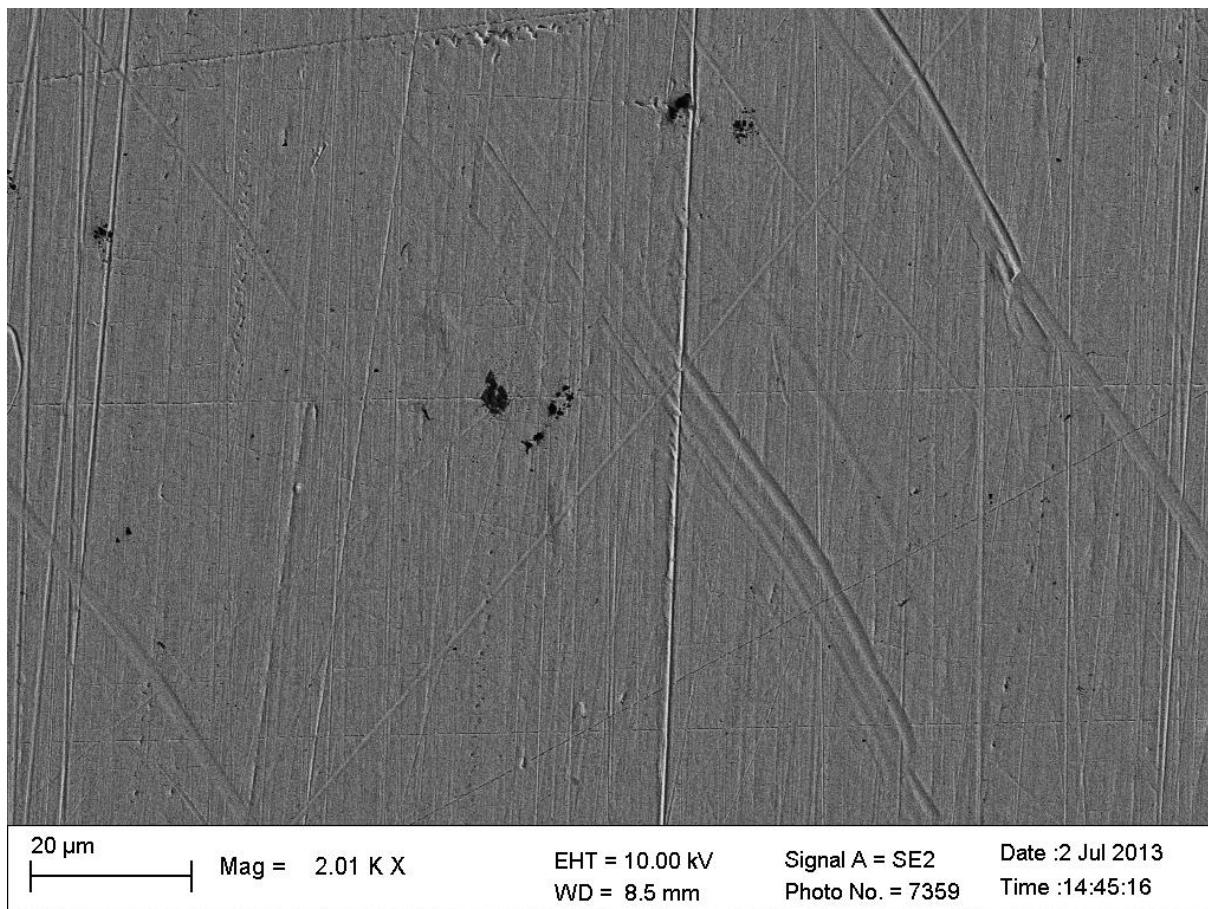

| 20 µm | Mag = 2.01 K X | EHT = 10.00 kV | Signal A = SE2 | Date :2 Jul 2013 |
| | | WD = 8.5 mm | Photo No. = 7359 | Time :14:45:16 |

Figure 6.7 SEM image of a surface of the reference sample: polished copper cube.

The surfaces of the copper cubes of the overnight experiment were analyzed at SEM, the preoxidized cube that presents black spots all over the surface was zoomed on the part of the surface that appeared visibly corroded.

A representation of the SEM analysis carried out on the copper cube samples involved in the overnight experiment follows below.

In the figure 6.8 is evident the presence of various local corrosion features with the appearance of a central circular area with many dots and holes inside.

| 100 µm | Mag = 87 X | EHT = 10.00 kV
WD = 8.6 mm | Signal A = SE2
Photo No. = 7395 | Date :2 Jul 2013
Time :15:47:36 |
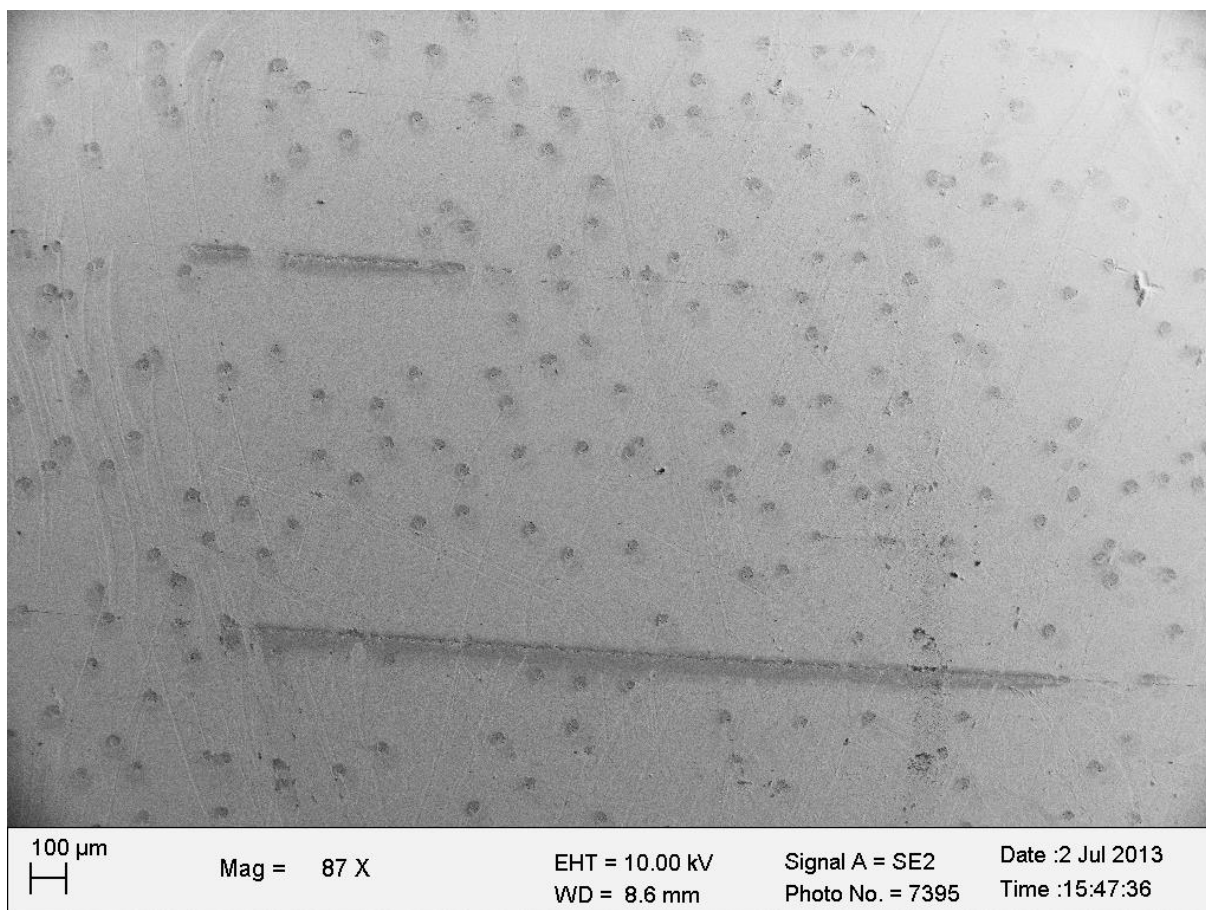
Figure 6.8 Polished copper cube exposed to a solution 5mM H_2O_2 : zoom out of the surface.

The corrosive signs of the polished copper cube surface exposed to the hydrogen peroxide solution are the same noticed on copper cube exposed to gamma irradiation (see chapter 2, figure 2.2b).

In order to better see these local corrosion features, some of the circular zones were magnified. In the following figures are shown some magnifications of the circular features where is possible to point out some holes and the small craters.
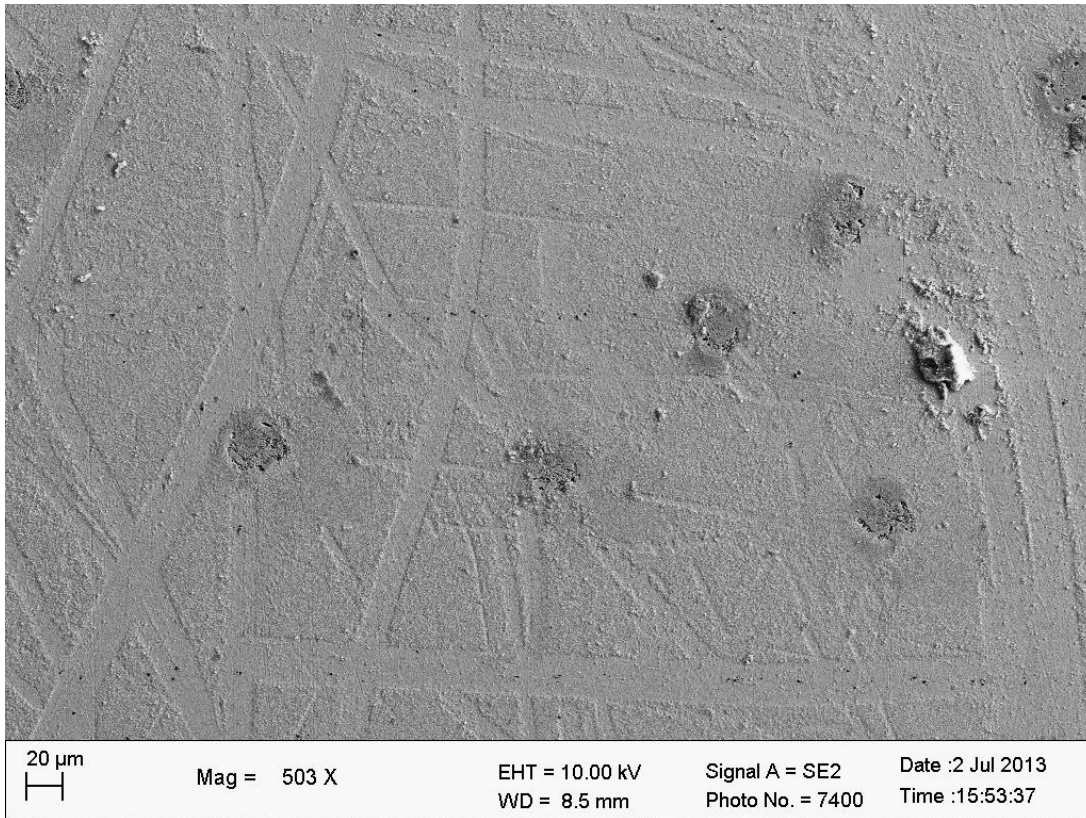
Figure 6.9 Polished copper cube exposed to a solution 5mM H_2O_2 : zoom in on the surface.
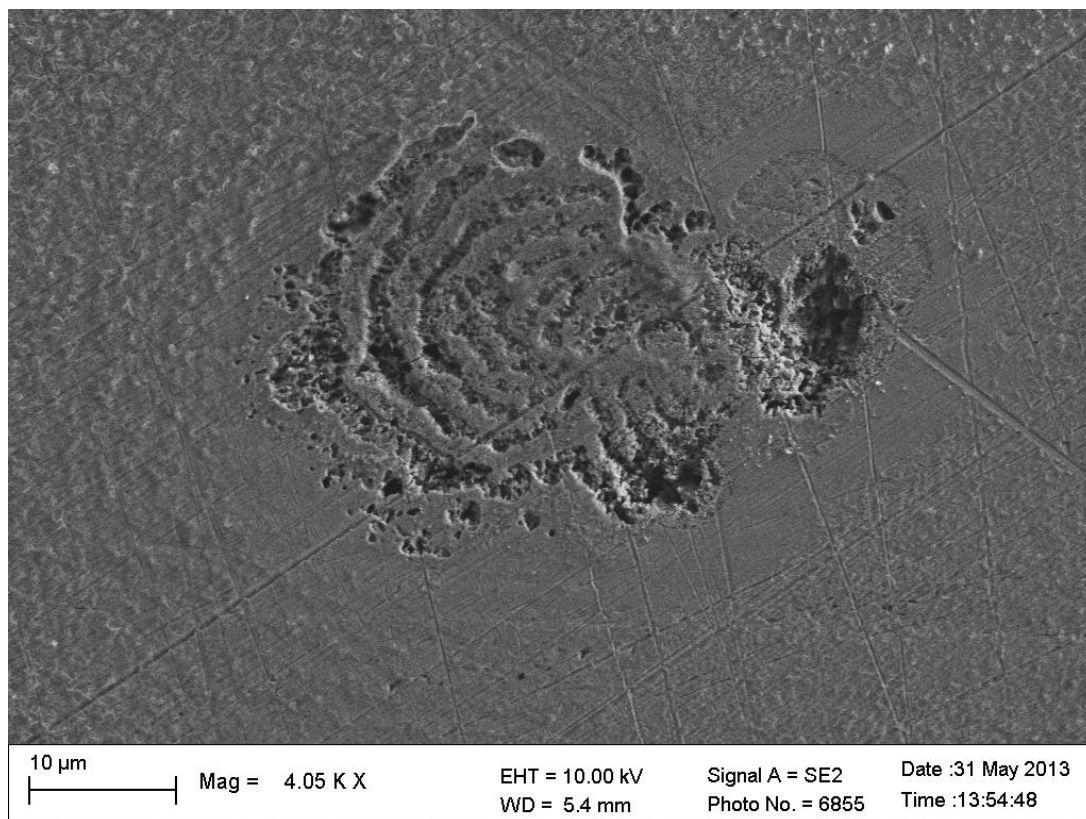

Figure 6.10 Polished copper cube exposed to a solution 5mM H_2O_2 : magnification of the circular corrosion feature

The figures 6.8 – 6.10 show the surface of the polished cube at the end of the experiment involving 5mM of hydrogen peroxide solution, even if the copper cube had no visible corrosion features on the surface, the SEM analysis shows that the surface presents many corrosion circular spots. The local corrosion circles are spread all over the surface, they are characterized by many dots and holes that present higher level of oxygen contents. The presence of oxygen in these regions represents a crystalline oxide layer formed in the craters observed with the electron microscope analysis. The corrosive reactions due to the contact of hydrogen peroxide with the polished surface of the copper cube is evident thanks to the SEM analysis.

After the SEM analysis on the surfaces of the polished cube exposed to the hydrogen peroxide solution, the same analysis was performed on the preoxidized cube inserted in the hydrogen peroxide reaction solution, the results achieved with the microscope are presented below.

| 100 μm | Mag = 87 X | EHT = 10.00 kV | Signal A = SE2 | Date :2 Jul 2013 |
| | | WD = 8.7 mm | Photo No. = 7373 | Time :15:10:05 |
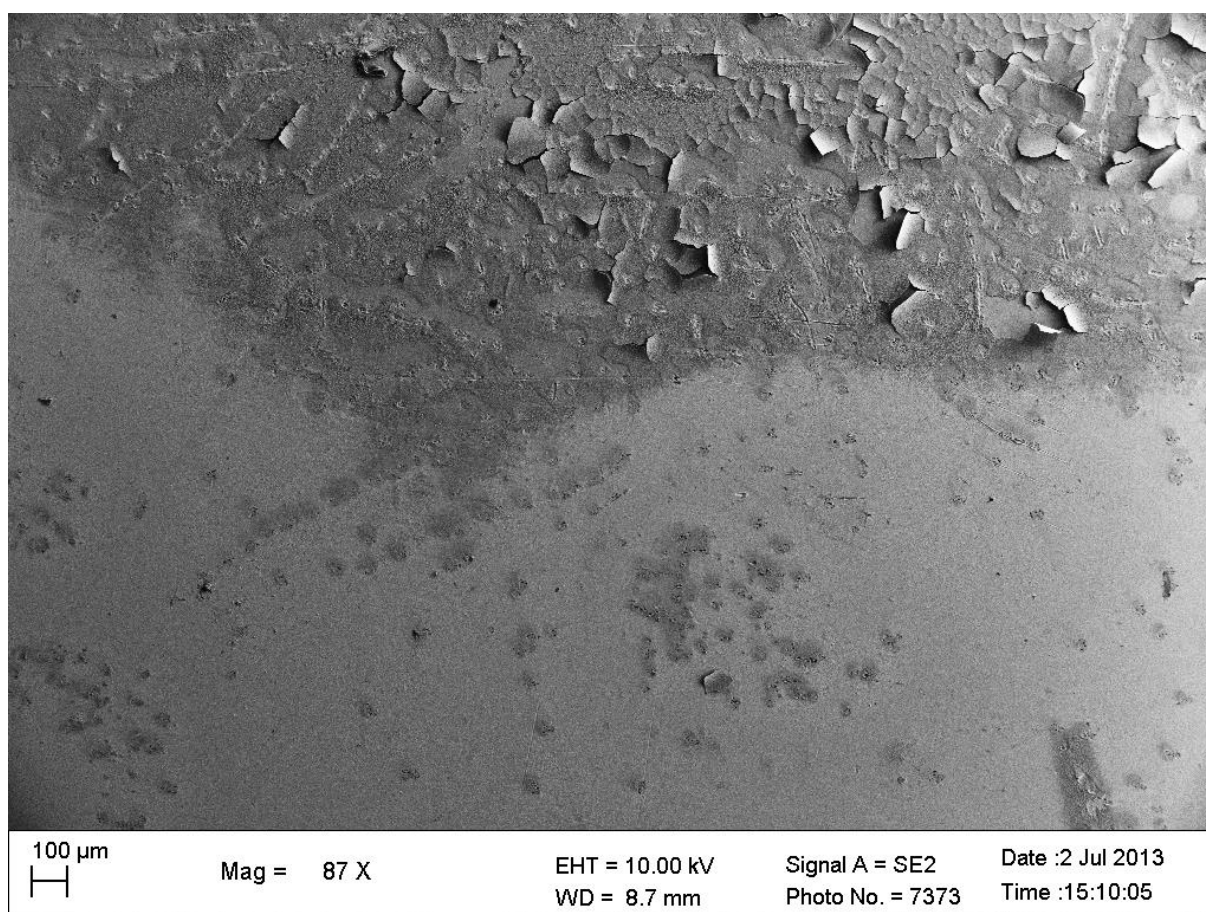
Figure 6.11 Preoxidized copper cube exposed to a solution 5mM H_2O_2 : zoom out of the surface

The picture 6.11 is a magnification of the preoxidized copper cube surface characterized by black and dark features. The visible corrosion features in the picture belong to the dark spots of the surface, they present peculiar characteristics that were not found in the previous images. The local circular corrosion features found in the polished copper cube after hydrogen

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peroxide experiment are here visible as well. The main difference regards the surface that presents breakages and grain damages in the oxide layer.

A better magnification of the corroded surface is presented below.

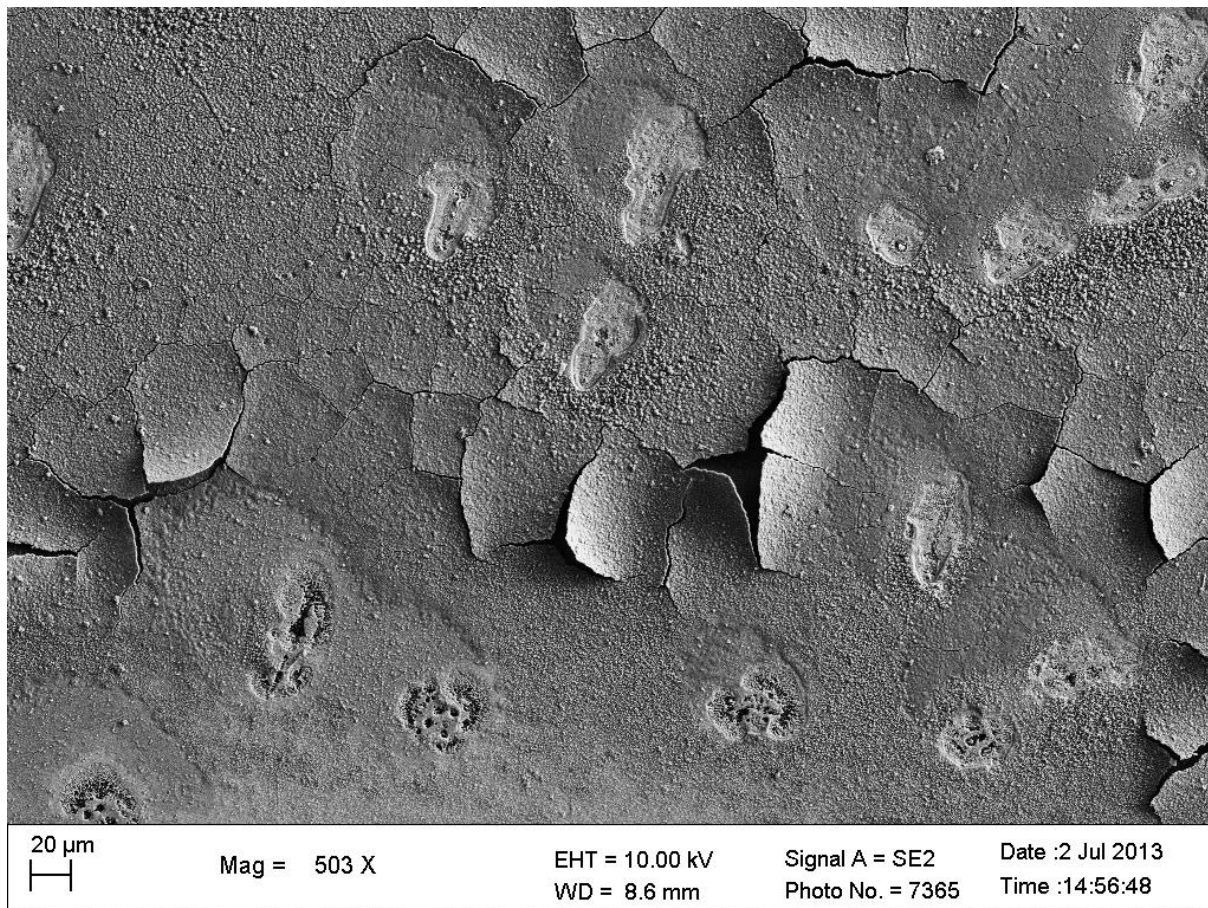| 20 μm | Mag = 503 X | EHT = 10.00 kV WD = 8.6 mm | Signal A = SE2 Photo No. = 7365 | Date :2 Jul 2013 Time :14:56:48 |

Figure 6.12 Preoxidized copper cube exposed to a solution 5mM H_2O_2 : magnification of the damaged oxide surface

In the figure 6.12 are evident the damages present on the copper oxide layer surface, the local corrosion features displayed as circular craters are the same found in the polished cube (see figure 6.9) but in the preoxidized cube sample there are also some grain breakages.

The appearance of this morphology is revealed as black dark spots displayed in figure 6.4 on the right side. From a visible point of view and based on the characterization of the surface with SEM, the preoxidized cube seems to be much more corroded. The presence of an oxide layer seems to reduce the integrity of the surface, the corrosion reactions go much in deep and affect the morphology of the surface .

In order to complete the experimental analysis and evaluate the action of the hydrogen peroxide solution in comparison with the hydrogen peroxide produced during the water radiolysis induced by radiation, some copper cubes were exposed to a hydrogen peroxide solution as previously done in the overnight experiment for the preoxidized cube. These cubes instead of being inserted in the reaction solution 5mM H_2O_2 were inserted in a glass beaker

with milliQ Millipore water and were put into the gamma source for 96 hours. It was previously shown in chapter 2 that the irradiation of the polished copper cubes sealed in water (figure 2.2 b) presents the same local circular corrosion features evaluated in figures 6.9 and 6.10 in the polished cube exposed to the hydrogen peroxide experiment. The results from this analysis are shown below.

100 µm   Mag = 85 X   EHT = 10.00 kV   WD = 8.7 mm   Signal A = SE2   Photo No. = 7384   Date :2 Jul 2013   Time :15:26:06
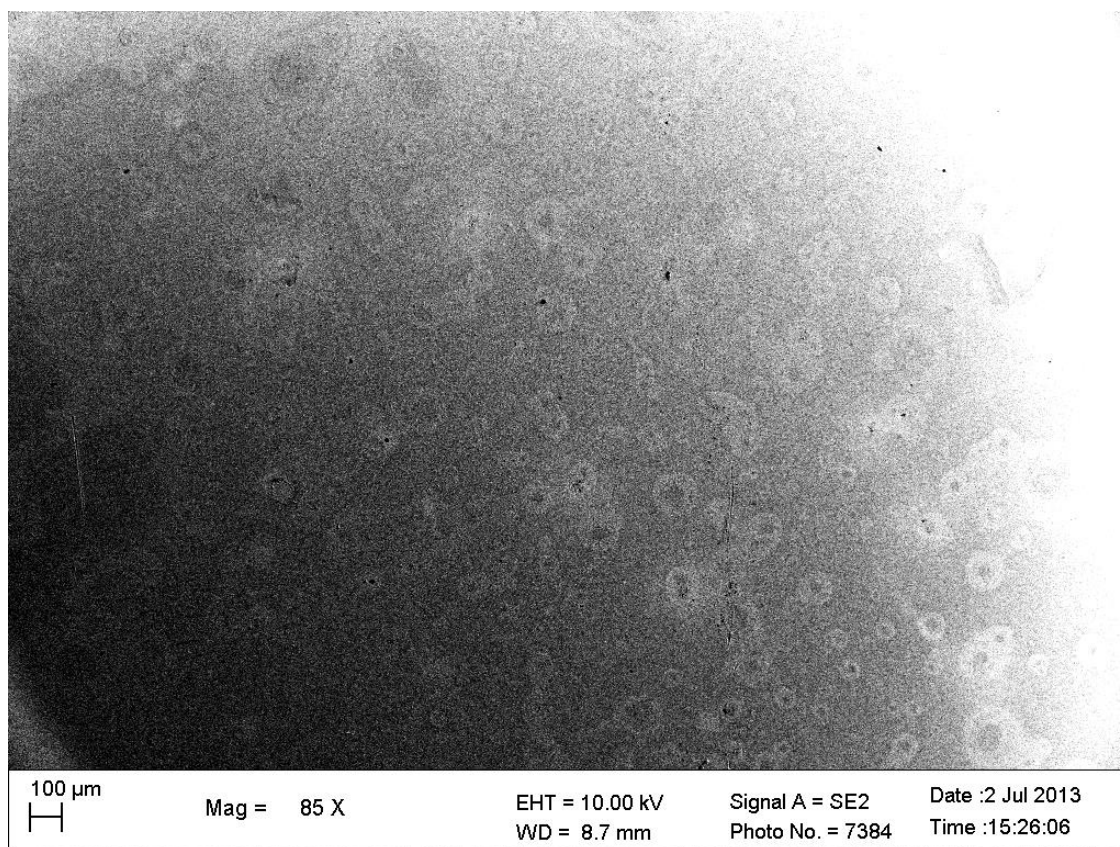
Figure 6.13 Preoxidized copper cube exposed to an irradiation session for 96 hours: zoom out of the surface.

The preoxidized irradiated copper cube surface in figure 6.14 shows the same local corrosion circular feature noticed in the figure 6.10, the morphology of the irradiated preoxidized copper cube is very similar to the one found for the polished copper cube exposed only once to hydrogen peroxide solution.

The purpose of this experiment is to evaluate if the effects produced by the hydrogen peroxide solutions used in the experiments performed is the same recorded on copper cube surfaces after the irradiation in the gamma source.

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Figure 6.14 Preoxidized irradiated copper cube: magnification on a circular corrosion feature

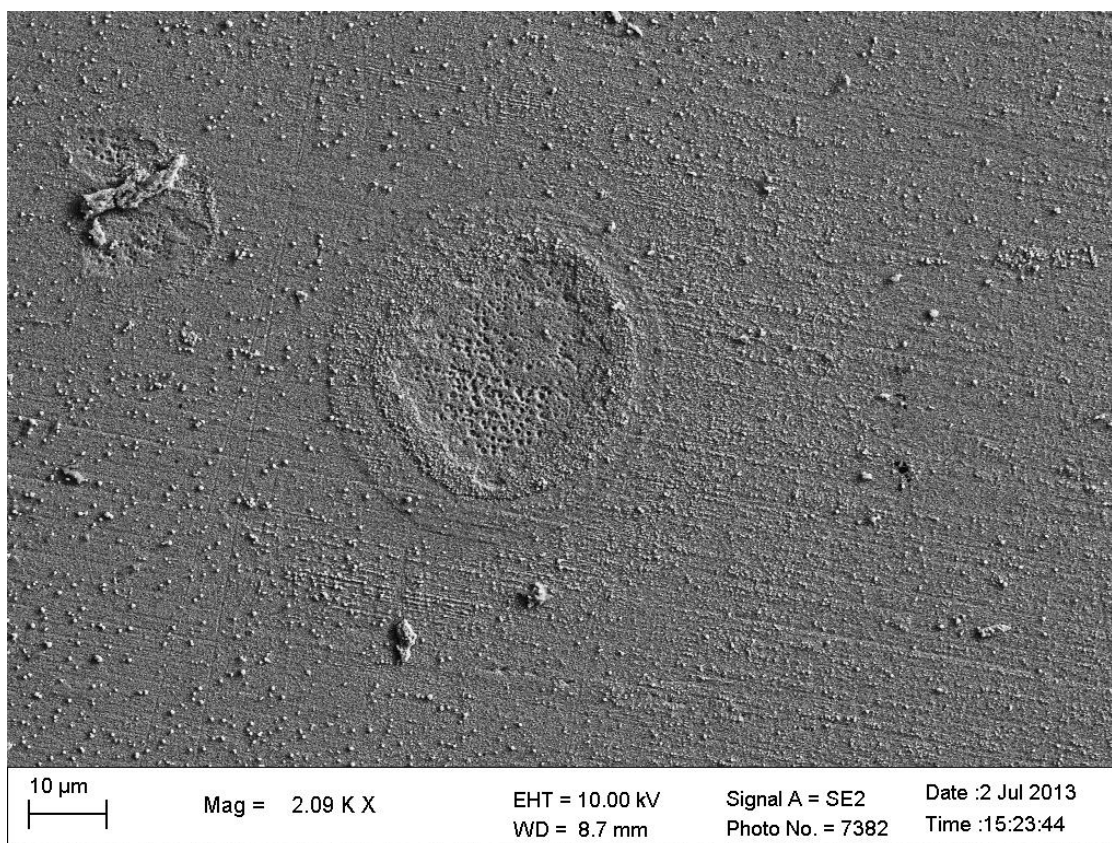From the SEM analysis seems that the presence of hydrogen peroxide in contact with an oxide layer damages the integrity of the surface much more than when the oxide layer is subject to irradiation. It has to be pointed out that the concentrations used in the hydrogen peroxide experiments (mM) have the same order of magnitude than the concentrations of hydrogen peroxide produced by water radiolysis during approximately 96 hours of irradiation. The accumulated concentration anyway is not given directly by the dose and the G-value (equation 7 pag.44) because H_2O_2 is consumed in other reactions. In order to quantify the copper corrosion in terms of copper releases in solution, an ICP analysis on every experiment was performed.

6.2.3 ICP Analysis

The results of experiments presented in the previous paragraphs demonstrate the crucial role of the oxidant species H_2O_2 as main responsible for the corrosion of the copper surface. The surface of the copper cube sample previously oxidized in an environment containing H_2O_2 was seriously corroded in presence of the hydrogen peroxide in the reactant solution, the surface presents superficial breaks besides the local circular corrosion features spread all over the surface.

In order to evaluate the damages produced by hydrogen peroxide on the surface to evidence the copper releases due to corrosion processes, the ICP analysis was carried out in the solutions of each experiment.

Table 6.1. *Results of ICP analysis on experiments performed with copper cube samples exposed to 100ml solution at 100mM CH₃OH, 3 or 5mM H₂O₂ or exposed to an irradiation session.*

COPPER CUBE SAMPLE PRETREATMENT	H_2O_2 (mM) Exp.	Cu (ppm)	Dose rates (Gy/s)	Total dose (kGy)
PREOXIDIZED CUBE in 2.5mM H_2O_2	-	0.19	0	0
POLISHED CUBE (n)	5	0.83	0	0
POLISHED CUBE (1)	3	1.09	0	0
POLISHED CUBE (2)	3	0.90	0	0
POLISHED CUBE	5	1.26	0	0
POLISHED CUBE	5	1.29	0	0
PREOXIDIZED CUBE (n) in 2.5mM H_2O_2	5	1.97	0	0
PREOXIDIZED CUBE (1) in 3mM H_2O_2	3	1.57	0	0
PREOXIDIZED CUBE (2) in 3mM H_2O_2	3	0.27	0	0
PREOXIDIZED CUBE in 2.5mM H_2O_2	-	10.23	0.100	35
PREOXIDIZED CUBE in 2.5mM H_2O_2	-	6.85	0.249	86
PREOXIDIZED CUBE in 2.5mM H_2O_2	-	6.89	0.134	46
PREOXIDIZED CUBE in 2.5mM H_2O_2	-	7.85	0.115	40

From previous studies were reported that polished copper cube samples irradiated in the gamma source for a certain period that goes from 80 − 114 hours presented copper releases within 2-3 ppm [16].

From the ICP analysis presented in table 6.1 is evident that the preoxidation process on the copper cube enhances the copper releases in solution in most of the cases. Others experiments were performed and the results were in line with the results reported in the table.

A polished cube exposed to an experiment at 5mM of hydrogen peroxide presents releases of copper in solution approximately 1 ppm, the oxide layer induced by the exposure of the polished cube in a solution with hydrogen peroxide protects the surface from further corrosive reactions, the result is that the copper releases are higher. It was however recorded an experiment in which the preoxidation of the sample protected the copper surface from further attacks (see preoxidized cube (2)), this is probably due to the fact that the oxide on the surface was homogeneous and shielded the inner surface from corrosion processes.

The strong correlation between concentration of H_2O_2 and copper releases in solution is shown in experiments with copper cube called (1) and (n). The preoxidized copper cube 1 reveals a slightly smaller amount of dissolved copper in solution compared to the one exposed at 5mM of H_2O_2 . Anyway it has to be pointed out that several experiments are necessary before understanding the whole process and give some clarifications to it.

The combination of preoxidation of the surface in cubes that are subsequently irradiated in the gamma source reveal the highest values of copper releases.

The oxidant species produced by the water radiolysis and the effects of the irradiation on a corroded surface are very crucial.

The releases are unexpectedly high, many others experiments with copper cube samples exposed to hydrogen peroxide at different concentrations would be interesting in order to evaluate the crucial role of an oxidant layer on the surface of the copper sample.

6.3 Conclusions

The experiments carried out with copper cube samples were various and revealed peculiar unexpected characteristics.

It was demonstrated that in most of the cases the formation of an oxide layer on the pure metallic copper surface weakens the material from further attacks of oxidant species. The corrosive processes were visible in experiments involving preoxidized samples, the dark features on the surface were an indications of the worse grade of corrosion of the surface. The visibly corroded sample revealed higher values of dissolved copper in solution, this is a sign that the oxide layer on the surface instead of shielding the material from further attacks it probably enhances some catalytic reactions that corrode the material. The worse grade of surface corrosion is revealed by dark spots all over the surfaces, from the breaks of the grain of the oxide layer evaluated with the SEM analysis and by the larger dissolved copper releases in solution evaluated with the ICP analysis.

All these results are an indication of the peculiar and critical role of the oxide layer, produced by the water radiolysis product H_2O_2 in contact with copper, on the corrosion resistance properties of copper.

Despite all the results previously discussed, one experiment, performed with a preoxidized cube inserted in an oxidant solution, showed a completely different behavior. In this case, reported as preoxidized cube 2, the oxide layer formed during the first exposure of the cube at hydrogen peroxide was able to shield the material from further corrosive attacks. The corrosion resistance of this sample was evaluated thanks to a visible analysis and from the ICP analysis that revealed a really low level of dissolved copper in solution. Unfortunately it was not possible to run the SEM analysis on its surface. The hypothesis made on this sample

is that in some cases the oxide layer produced on the copper surface is homogeneous enough to protect the material from further oxidative reactions.

The behavior of copper canister samples in contact with an anoxic aqueous environment in which are present products from water radiolysis is not yet well understood.

After this experimental session other experiments were planned in order to investigate the surfaces of the samples that present an inert behavior to evaluate the morphology of the oxide layer of the surface.

One of the difficulties of the characterization of the copper surface behavior is that is quite complicated the characterization of the oxide layers formed on the surface during experiments performed with hydrogen peroxide or after an irradiation session. The results made so far reveal that the most important oxide formed on copper surface is the copper (I) oxide, and because of this was carried out the experimental session on copper oxides previously shown.

The role of the homogeneous oxide layer in shielding the material from corrosive attacks needs further experimental validation. One of the possibilities for the future experiments would be the formation of a homogeneous oxide layer on copper cube samples before the experimental session with hydrogen peroxide solutions.

Other experiments are needed to be performed in order to clarify some uncertain aspects, they will involve copper cube samples exposed to different amounts of hydrogen peroxide and then irradiated.

Thanks to hydrogen peroxide experiments involving samples exposed to 3mM of H_2O_2 it was demonstrated that there is a strong correlation between concentration of hydrogen peroxide in the system and dissolved copper releases as shown for the copper cube 1, it is anyway necessary to collect many other results in order to give clarifications on this process.

This analysis demonstrates that possible oxidative processes can occur on the copper canister surface in an anoxic aqueous condition, due to the presence of hydrogen peroxide formed during the radiolysis of water. This oxidant species is able to create an oxide layer on the surface of the copper that is able to further affect the stability and the corrosion resistance properties of the copper canister. The analysis is not conclusive as it was reported an example of absolute stability of a copper cube sample due to the presence of an oxide layer formed on its surface after hydrogen peroxide exposure.

Chapter 7

Evaluation of the reaction kinetics of copper

All the experimental data collected during the experimental session performed in this work involving copper oxides powder, copper powder and copper cube samples are analyzed in order to determine the reactions occurring in each system.

The data processing brought some relevant results on the hypothesis of mechanism of reaction made on copper in contact with hydrogen peroxide. The kinetics of consumption of H_2O_2 and formation of CH_2O for each material are explained and compared.

7.1 Comparison on copper and copper oxide powders experimental data

All the results gained in experiments performed with the copper powder and the copper oxide powders were set for the investigation of the reactivity of hydrogen peroxide. The analysis on these materials had the purpose to better understand the mechanism and pathways reaction that occur when a molecule of hydrogen peroxide enters in contact with the copper surface.

This investigation is focused on the effects of radiation induced corrosion on copper canisters used in the KBS-3 concept, the hydrogen peroxide is considered the most oxidant species produced by radiation in contact with water. The experimental data obtained in the copper canister experiments showed a complex behavior of the kinetics of consumption of H_2O_2 in contact with the pure copper surface. In order to better understand the reactivity of copper towards hydrogen peroxide, an experimental analysis involving the copper in shape of oxide (I), cuprite, and (II), tenorite, was set. The experiments performed on the surfaces or suspensions of the copper materials show a peculiar behavior of this species in contact with the different surfaces.

The data obtained regarding the kinetics of consumption of H_2O_2 were analyzed first with a logarithmic analysis in order to demonstrate the catalytic decomposition of hydrogen peroxide on the surface as a possible pathway of decomposition of this species. This reaction is indeed supposed to follow a first order kinetics. The analysis with this method is able to evaluate a pseudo first order rate constant that describes the reactivity of hydrogen peroxide on the surface of the material considered.

In the next graphs the analysis of the kinetics found in experiments performed with the copper and copper oxide powders are shown, the shape in powder allows a suitable method to perform experiments at different conditions.

The tenorite powder reveals a simple first order mechanism of reaction, the experiments at different quantities of powder allow the evaluation of the first order rate constant as a function of mass.

The cuprite powder experiments reveal a much complex reactivity of H_2O_2 in contact with the powder, the logarithmic analysis does not give reliable values for the first order rate constant so another way to rearrange the results was used.

The complexity of the system with regards to the oxidative process due to hydrogen peroxide in contact with copper increases as it can be seen in copper experiments. The data were analyzed in a different manner compared with the oxides powder analysis, the results achieved follow in the next section of this chapter.

7.1.1 Tenorite powder Analysis

The copper II oxide powder, tenorite, shows a first order kinetics of the decomposition reaction of hydrogen peroxide with respect to H_2O_2 in every experiment performed.

Every experiment involving the tenorite powder in contact with a certain amount of hydrogen peroxide, that is 5 mM, shows a good agreement between the experimental data treated with the logarithmic analysis.
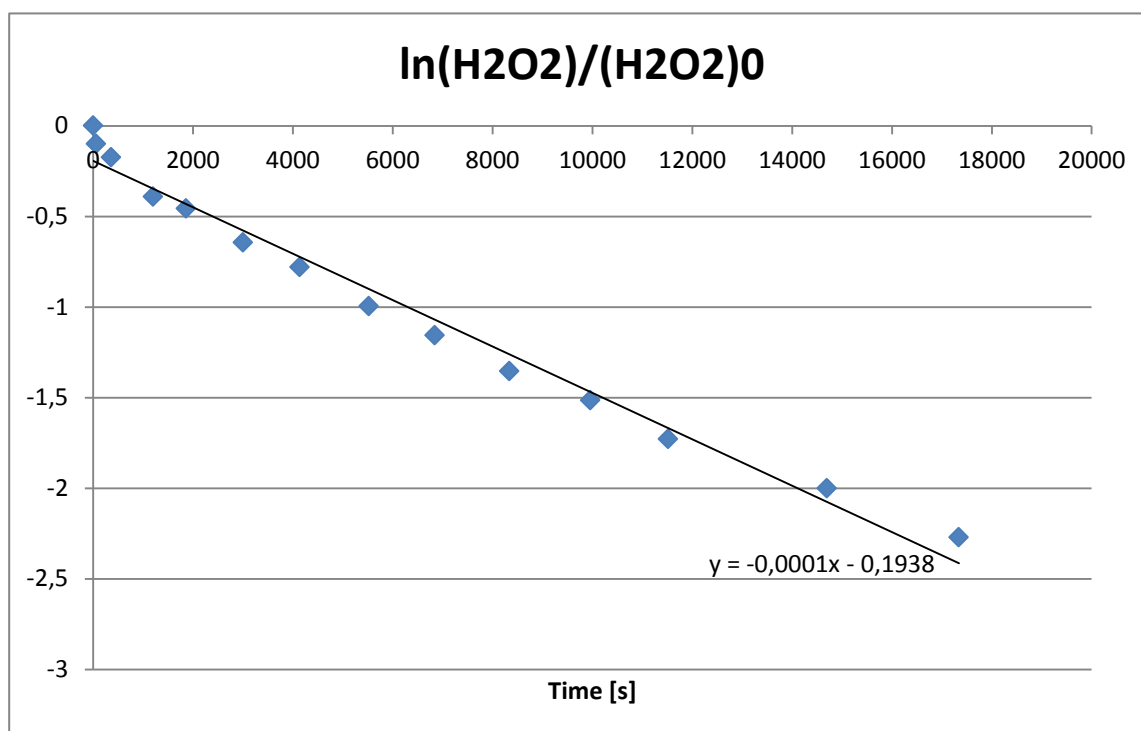

Figure 7.1 Copper (II) oxide 16 July experiment, mass 0.01 gr: $\ln([H_2O_2]/[H_2O_2]_0)$ as a function of reaction time

90

The set of data obtained during the sampling, were analyzed with respect to a pseudo first order analysis. An example of the logarithmic analysis made on the concentrations of hydrogen peroxide as function of reaction time is reported in the graph above.

As it can be seen from figure 7.1 the assumption of pseudo first order kinetics with respect of H_2O_2 in the copper (II) oxide experiment is a good hypothesis. This analysis was carried out in each experiment performed and in all of them the assumption of the first order kinetics was satisfied.

The experimental data of each graph are well represented by a straight line with a characteristic slope coefficient. The experiments with tenorite powder were performed at different powder amounts within a mass range of $0.01 - 0.15$ grams.

The evaluation of the first order rate constant as a function of the mass amount of copper (II) oxide gives important information regarding the behavior of the hydrogen peroxide consumption reaction.

The pseudo first order rate constants evaluated for each experiment are further presented as a function of mass in the figure 7.2.
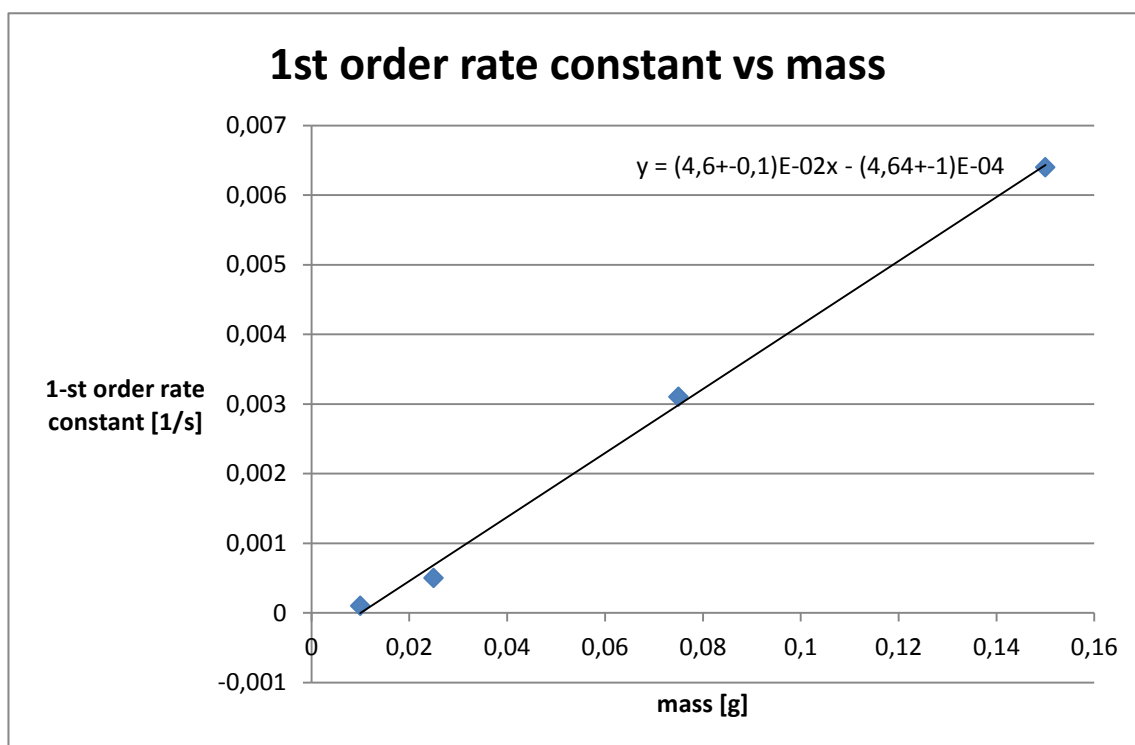

Figure 7.2 First-order rate constant as a function of copper (II) oxide mass obtained in experiments at room temperature at initial concentration of 5mM in H_2O_2 100mM CH_3OH in a volume of 100 ml

In figure 7.2 all the pseudo first order rate constants were plot against the powder mass amount used in the experiment. The relation between rate constants and mass is displayed as a straight line that approximates really well the data with a slope of $(4,6 \pm 0,1) \cdot 10^{-2}$ (g·s)$^{-1}$.

For heterogeneous reaction where the reaction follows a first order kinetics, it would be possible to determine the second order rate constant studying the variation of the k_1, first order rate constant evaluated with reactions (5) and (6) (see paragraph 3.2.3), as a function of solid surface area to solution volume ratio.

$$\frac{-d\,[H2O2]}{dt} = k\,[H2O2] \quad (5)$$

$$ln\frac{[H2O2]}{[H2O2]0} = -k\,t \quad (6)$$

Indeed the reaction through which is possible to evaluate the second order constant is:

$$\frac{-d\,[H2O2]}{dt} = k2(\frac{S}{V})\,[H2O2] \quad (8)$$

where k_2 is the second order rate constant, S is the surface area of the solid and V is the solution volume.

In this case the reaction considered is indeed an heterogeneous reaction because a solute, hydrogen peroxide, is involved reacting with an aqueous particle suspension of copper (II) oxide.

The second order rate constant can be determined through the analysis of the plot of the first order rate constant as a function of solid surface area to solution volume ratio (S/V). In this case the second order rate constant k_2 has units of $(m \cdot s)^{-1}$.

During the planning of experiments was set an experimental session with B.E.T. (Brunauer-Emmett-Teller Surface Area Analysis) for all the powders involved. The B.E.T. is necessary for the estimation of the surface area of the powder, thanks to the value of each powder surface area it would be possible the evaluation of the second order rate constant. Unfortunately it was not possible to perform this analysis as the instrument was not available, the second order rate constants are not evaluated but the estimation of the typology of reaction is made considering the first order rate constants as function of mass involved.

From figure 7.2 it is evident that the straight line describing the experimental data has an intercept that cross the zero point of the axis. The characteristic of the straight line means that in experiments in which no powder is inserted in the reaction vessel the extrapolated behavior of the tenorite powder has a first order kinetics constant equal to zero and so that no reaction takes place.

The direct dependence of the rate of consumption and the amount of powder inserted in the reaction vessel is due to an occurrence of a surface reaction. The reaction of decomposition of hydrogen peroxide occurs as a surface reaction, indeed when the mass approaches to zero

there is no kinetics of the reaction. The consumption of hydrogen peroxide only depends on the amount of powder in solution, so that the trend of kinetics of the hydrogen peroxide is directly dependent on the surface area involved.

A surface reaction of first order kinetics which is responsible of the consumption of hydrogen peroxide is indeed the metal oxide catalyzed reaction. The hypothesis of this pathway reaction was previously reported in the mechanism (1) as equation R3:

$$H_2O_2\ (aq)+ M^{\ y}(s) \longrightarrow 2HO\cdot(ads)/(aq) + M^y\ (s)$$
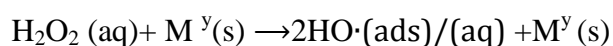
The results achieved with this analysis show that this mechanistic pathway is mainly the only reaction that take place on tenorite surface. The reason because the hydrogen peroxide reacts on copper (II) oxide surface only via this way is because the copper (II) oxide is at highest level of oxidation. The system considered is the simplest one regarding the copper materials involved in this analysis as the powder is at the highest stage of oxidation, so it reacts in only one way when it is in contact with the oxidant.

Thanks to the tenorite experimental session it is verified the proposed mechanism of reaction of hydrogen peroxide in contact with a metal oxide, that is the metal oxide catalyzed reaction.

7.1.2. Cuprite powder Analysis

The copper (I) oxide experimental session shows a completely different behavior of the powder in contact with the hydrogen peroxide with respect to the tenorite results. The experiments were performed in the same way of the tenorite powder ones and in both cases is evident the correlation between amount of powder and reactivity towards hydrogen peroxide. Increasing the powder amount in the reaction vessel, namely the surface area, the consumption of hydrogen peroxide in the system is faster.

The kinetics of consumption of H_2O_2 in the cuprite system does not show a pseudo first order behavior on the contrary. The logarithmic analysis was carried out in each experiment performed, an example is shown in the graph below for an experiment performed with cuprite powder.
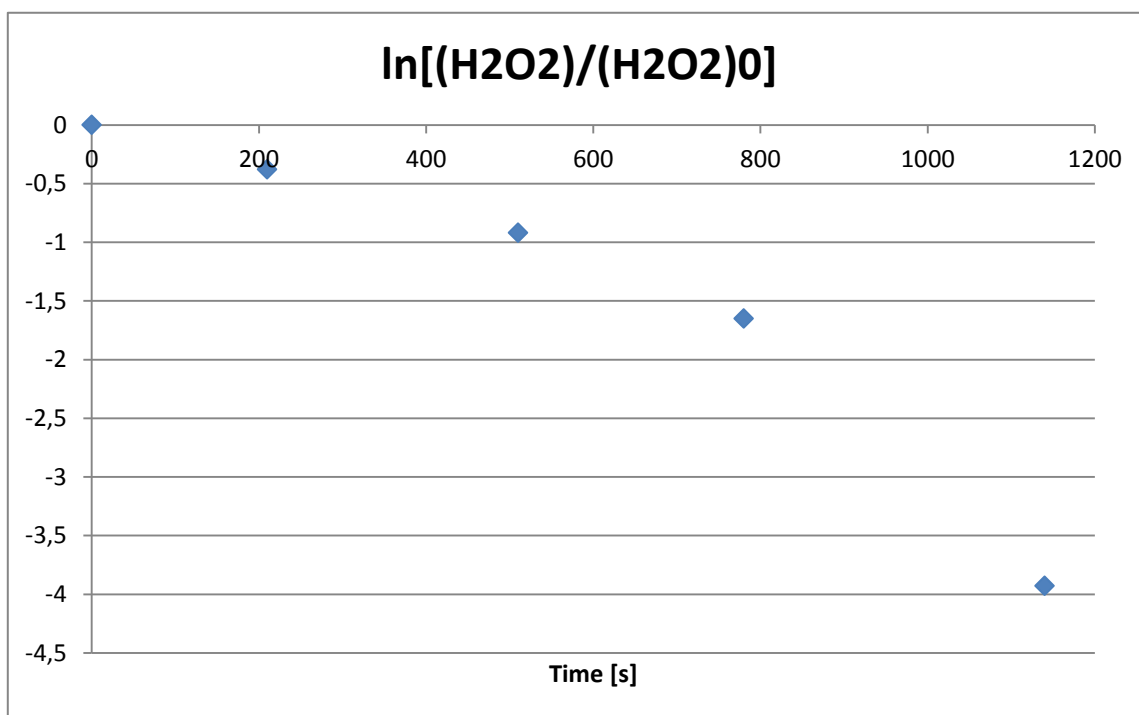
Figure 7.3 Copper (I) oxide 9 September experiment, mass 5gr: $\ln([H_2O_2]/[H_2O_2]_0)$ as a function of reaction time

As it can be seen from figure 7.3 the experimental data have a trend that cannot be well represented with the approximation of a first order kinetics of reaction. Every experiment shows a trend of consumption of H_2O_2 that presents a faster reactivity at the beginning that decreases during the experiment.

The impossibility to consider the kinetics of consumption of hydrogen peroxide as a pseudo first order reaction makes not possible the evaluation of the first order rate constants.

The analysis of the surface area, as already said, was not possible to run. In order to compare and analyze the results achieved in the cuprite experimental session with the results gained with copper and tenorite, the evaluation of the initial rate constants was performed.

In each experiment performed, it was necessary to evaluate the rate of reaction with respect to H_2O_2. Considering the first three sampling data it was evaluated the initial rate constant of the reaction of consumption of hydrogen peroxide in each experiment.

The initial rate is calculated as the slope coefficient of a straight line that connects the first three points of the graph.

The initial rate constants are further plotted against the mass involved in the experiments, as it can be seen in graph 7.4 in the next page.
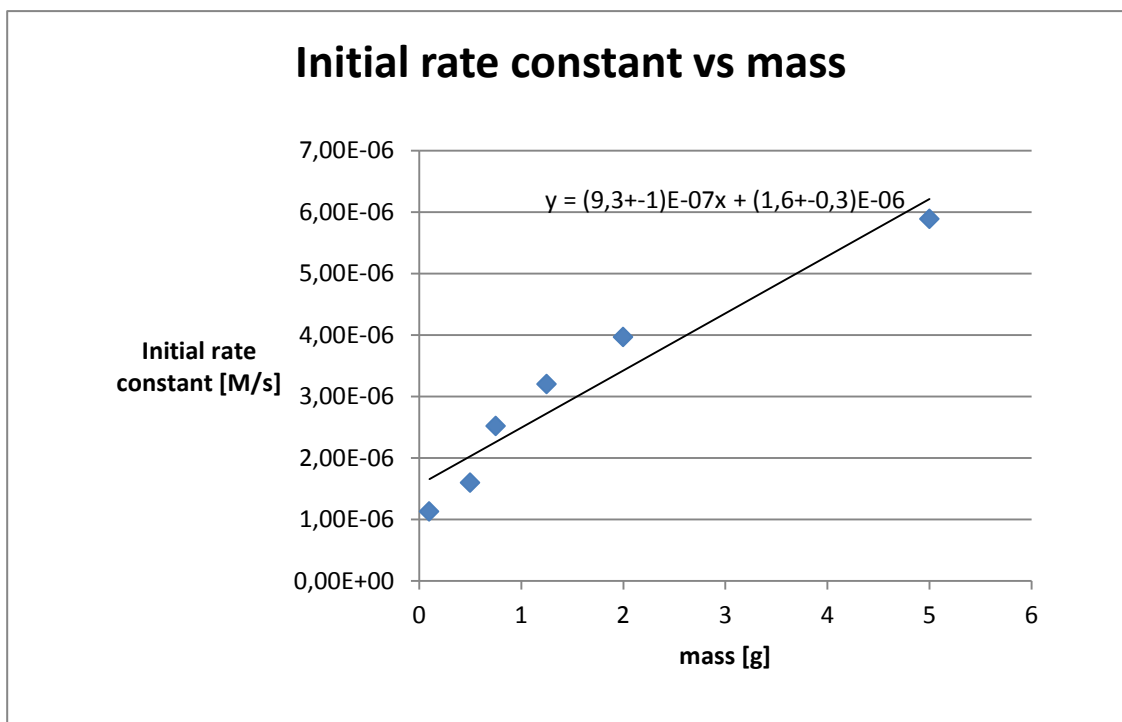
Figure 7.4 Initial rate constant as a function of copper (I) oxide mass obtained in experiments at room temperature at initial concentration of 5mM in H_2O_2 100mM CH_3OH in a volume of 100 ml.

The graph of the initial rate constants versus mass allows a discussion that compares the data obtained with the copper (II) oxide powder.

The straight line that describes the experimental data has a slope of $(9,3 \pm 1) \cdot 10^{-7} \, M \cdot (g \cdot s)^{-1}$ and an intercept of $(1,6 \pm 0,3) \cdot 10^{-6} \, M \cdot (s)^{-1}$.

On the contrary of what was previously described, the straight line presents an intercept that is far from the zero point. The presence of an intercept value means that for a value of mass powder that approaches to zero in solution there should be still a kinetics of reaction that is not strictly dependent on the powder amount. The discussion previously reported showed that the kinetics of decomposition related to the slope of the straight line is due to a surface reaction that is strictly related to the surface area of the powder in contact with the hydrogen peroxide solution.

The intercept of the straight line in the graph represents a kinetics of reaction that is independent from the powder amount diluted in solution. The independence of the kinetics of the reaction from the powder amount in the system can be explained with the assumption of a reaction that does not occur on the surface of the material.

The difference between the two copper oxide systems is the level of oxidation of the powder considered. The cuprite is at first level of oxidation and therefore the copper Cu (I) can be further oxidized into Cu (II) in contact with a hydrogen peroxide solution, the tenorite powder instead in contact with a molecule of H_2O_2 reacts only via catalytic decomposition.

In order to better understand the kinetics of reaction between copper and hydrogen peroxide, some literature papers were studied. From previous works has been demonstrated that the copper Cu (I) in contact with H_2O_2 resulting in formation of HO· via a "Fenton − like" reaction [1].

This reaction has been reported in literature as:

$$Cu\ (I) + H_2O_2 \rightarrow Cu\ (II) + HO· + OH^- \quad (9)$$
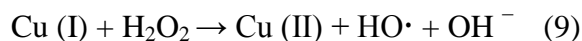
From the so called "Fenton − like" reaction is evident that the presence of the Cu (I) in contact with hydrogen peroxide produces hydroxyl radicals. In order to evaluate the influence of this possible reaction pathway in the system studied in this work, it is necessary to have the kinetics of the reaction.

From literature the rate constant for reaction of Cu (I) with H_2O_2 is $79 \pm 6\ M^{-1}s^{-1}$ [23], in order to understand if this reaction has a main role in the system of cuprite, a calculation of the rate constant from the figure7.4 is required.

The rate of reaction was difficult to evaluate as the assumption of a pseudo first order kinetics is no longer valid in the cuprite system. Instead of calculating the rate of reaction, from the figure 7.4 the intercept of the straight line is considered to be the rate of reaction involving the Cu (I) in the system. As previously said the reaction that is represented by the intercept is not related to a surface reaction, this means that the reaction between the Cu (I) and hydrogen peroxide should occur in the solution.

In the cuprite system are therefore present two reactions: the surface reaction which involves the H_2O_2 in contact with the copper (I) oxide powder, and a reaction that is powder amount independent and therefore is an homogeneous reaction in solution.

The surface reaction has already been demonstrated to be the metal oxide catalytic decomposition, that is present also in the tenorite system, while the homogeneous reaction responsible of the presence of an intercept in the figure 7.4 has to be evaluated.

The purpose of the evaluation of the rate constant of the cuprite homogeneous reaction is to compare this value with the rate constant evaluated for the "Fenton − like" reaction.

The rate of reaction of consumption of hydrogen peroxide is defined as the second order rate constant times the concentration of hydrogen peroxide in solution multiplied the surface to volume ratio (8).

In this case the equation (8) is rearranged in order to consider a homogeneous reaction, instead of considering the surface to volume ratio that is of crucial importance in a surface reaction, here it is considered the solubility of copper Cu (I) in solution.

The equation which is considered to describe the homogeneous reaction in the copper (I) oxide system is:

$$\frac{-d\ [H2O2]}{dt} = k3[\ Cu(I)]\ [H2O2] \quad (10)$$

Instead of considering the rate of reaction, in the left side of the equation (8) is used the intercept value of the straight line in the graph 7.4 that represents the presence of an homogeneous reaction in the system.

The solubility of copper (I) oxide was reported in literature to be approximately 3 μM [19], the homogeneous reaction which should take place between H_2O_2 and the copper (I) in solution considers the copper (I) ions dissolved in solution. The molecule of cuprite is Cu_2O and its solubility into water at room temperature is almost 3 μM, so the concentration of the Cu(I) dissolved in solution is considered to be approximately 5 μM. The concentration of hydrogen peroxide in solution is 5 mM.

The calculations made in this way reveal a rate constant of 64 M^{-1} s^{-1} for the cuprite experimental session. This value for the k_3 is close to the value found in literature that considers the "Fenton – like" reaction $k_{Cu(I) + H2O2} = 79 \pm 6\ M^{-1}\ s^{-1}$ previously reported.

The agreement between the experimental analysis and the literature value proves that in a system in which there is the presence of the copper (I) oxide, two reactions compete.

The homogeneous reaction is solubility dependent and gives always the same rate, the surface reaction is surface to volume ratio dependent and it is the most important one in a system with a considerable amount of mass. The much higher level of complexity of the cuprite system regarding the experimental data results is due to the presence of several reactions at the same time.

From the analysis of the initial rate constants versus mass was possible to evaluate that the copper (I) oxide reacts with the hydrogen peroxide via different pathways that involve surface redox oxidations and catalytic decomposition. The presence of many reactions in the same system makes difficult the analysis of the experimental data. The production of formaldehyde in the system has not a clear trend considering the surface area involved in the system. This is due to the fact that the hydroxyl radicals are not produced only via catalytic decomposition, as was the case of the tenorite powder, but they are involved in others oxidative processes.

7.1.3. Copper powder Analysis

The copper powder experiments were performed at same conditions used for the copper oxide powders. Nevertheless the results gained are much difficult to analyze than the experimental data of consumption of H_2O_2 and production of formaldehyde evaluated for copper oxides.

In each experiment performed was not possible the approximation of a pseudo first order kinetics of the reaction of decomposition of H_2O_2 this means that in the system not only the catalytic decomposition of hydrogen peroxide occurs.

As it can be seen from the graph 7.5 in the next page the experimental data of hydrogen peroxide does not follow a pseudo first order kinetics.
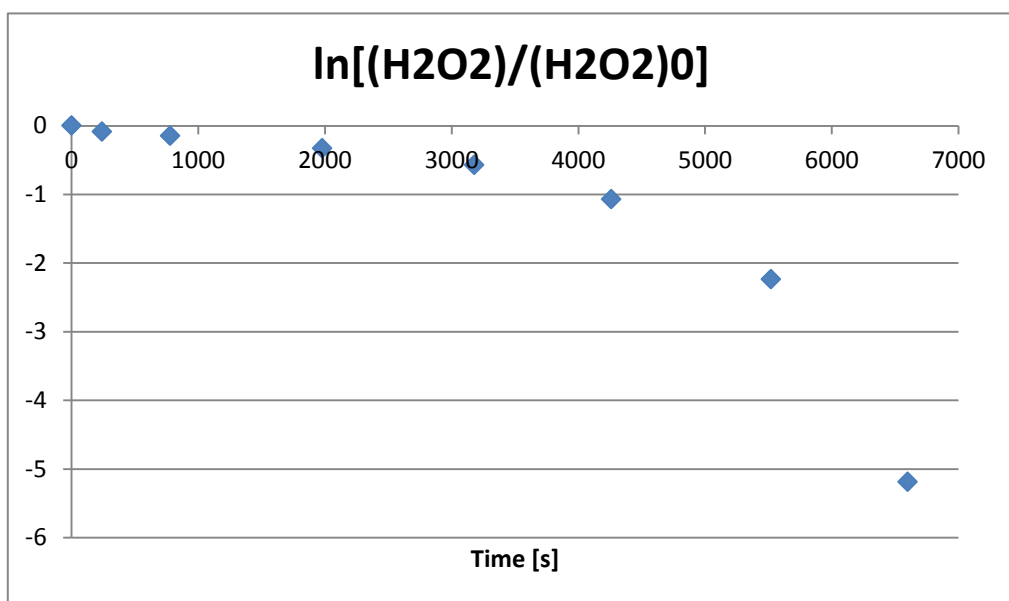
Figure 7.5 Copper powder 18 July experiment, mass 1gr: $\ln([H_2O_2]/[H_2O_2]_0)$ as a function of reaction time

The impossibility of the evaluation of the first order rate constants in the copper powder system, as for the cuprite, is followed by the analysis of the initial rate constants.

The procedure used for the evaluation of these constants is the same previously described for the cuprite powder.

The initial rate constants are then plot against the mass amount used in the experiment, the graph is shown in figure 7.6.
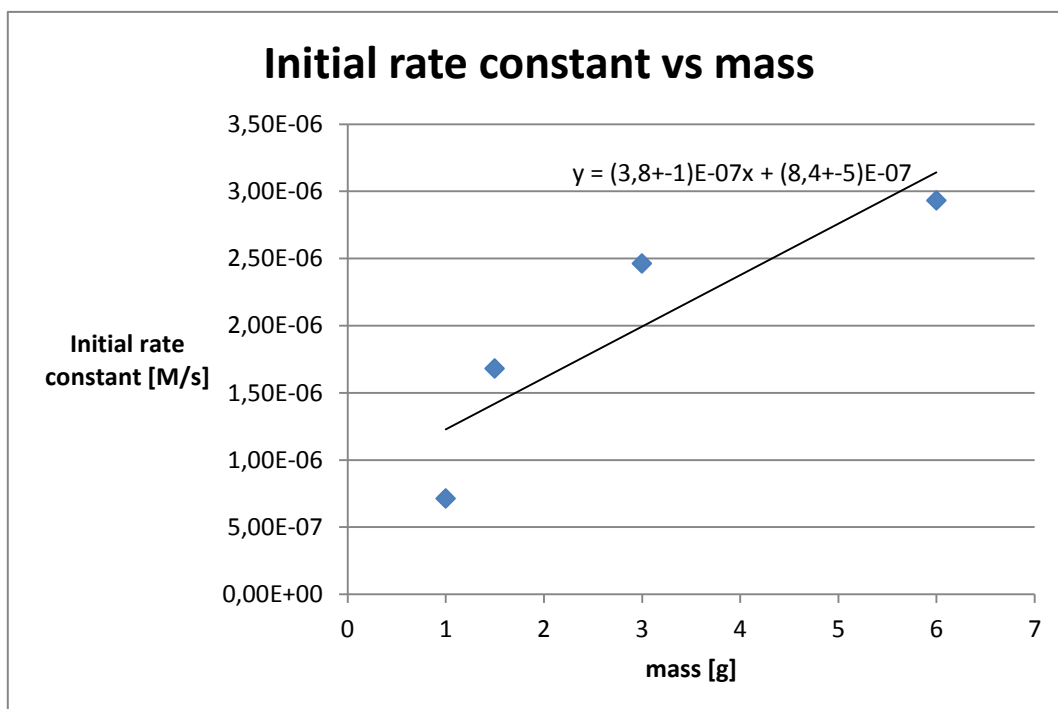

Figure 7.6 Initial rate constant as a function of copper powder mass obtained in experiments at room temperature at initial concentration of 5mM in H_2O_2 100mM CH_3OH in a volume of 100 ml

The plot shows a much complex behavior of the data, it is not possible to describe the trend of the initial rate constants versus mass with a straight line. The analysis with the straight line was performed in order to analyze all materials with the same procedure. It is evident that the complexity of the copper powder system has further increased with respect to the cuprite analysis, a different approach to the experimental data is used, as it can be seen in figure 7.7.

More reactions occur in the system, in order to better understand the reactivity of copper in contact with hydrogen peroxide the different reactions have to be identified separately.

To analyze the system in a similar way that was previously reported for the cuprite system, it is necessary to evaluate the contribution of the homogeneous reaction, if it is present as well.

The analysis with a linear trend gives an approximate description of the experimental data, in the figure 7.7 is used a logarithmic analysis.

In both the plots is important to see that an intercept of the line which describes the data is present, this means that the reactions involving the copper in contact with H_2O_2 are not only surface reactions depending on the surface area exposed to the oxidant. There is the presence of the homogeneous reactions which is mass independent.

The homogeneous reaction considered is the "Fenton – like" reaction, which considers the copper (I) dissolved in solution that reacts with hydrogen peroxide producing hydroxyl radical and copper (II), equation (9).

The same calculations performed for copper (I) oxide are used in this case, thanks to equation (10) is possible to evaluate the rate constant for the copper powder system. The concentration of hydrogen peroxide is 5 mM and the solubility of Cu(I) in solution is again 5 μM.
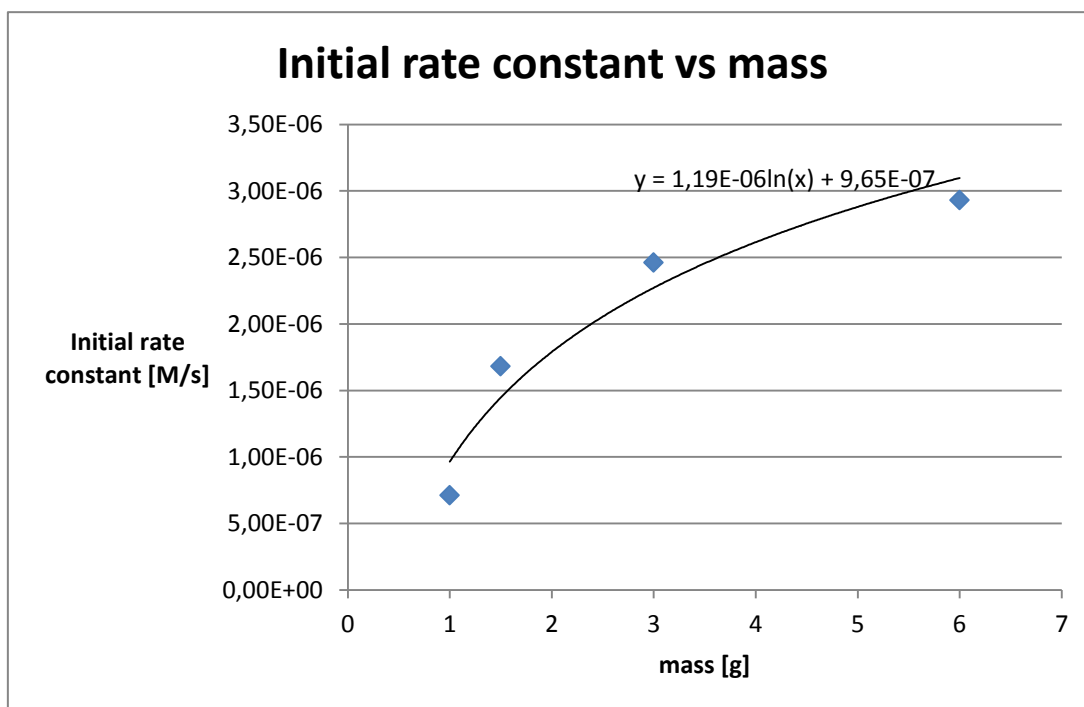

Figure 7.7 Initial rate constant as a function of copper powder mass obtained in experiments at room temperature at initial concentration of 5mM in H_2O_2 100mM CH_3OH in a volume of 100 ml

By applying the equation 10) in the copper case, the kinetics constant of copper powder experiments is evaluated.

The calculations on copper powder shows a rate constant of 38 $M^{-1} s^{-1}$, this value is much lower than the one found in the cuprite system which is indeed 64 $M^{-1} s^{-1}$. The value of the rate constant of the "Fenton – like" reaction $k_{Cu(I) + H2O2} = 79 \pm 6\, M^{-1} s^{-1}$ is almost the double of the one found in the copper system.

In literature no others reactions involving copper and hydrogen peroxide are found. The lower value of the constant rate is due to the fact that in a system in which pure metallic copper in solution is inserted, the formation of the Cu(I) is dependent from the process of oxidation of the copper. The lower value of the rate constant can be due to the fact that the process of dissolution of Cu(I) in solution is slowed by the effective process of formation of Cu(I).

The reactions that are present in the copper powder system are probably the same that were investigated in the cuprite system, plus the reactions that involve the pure metallic copper in contact with hydrogen peroxide and hydroxyl radical.

The processes of oxidation are more complexes and make difficult the full understanding of the kinetics of reactions of the H_2O_2.

7.1.4. Copper cube samples Analysis

The previous analysis involving the copper oxide powders and the pure copper powder had the purpose of simplifying the complex system of the copper metallic surface in contact with hydrogen peroxide in order to understand which are the most important reactions that take place and can affect the reactivity of the material.

The previous studies showed that many reactions occur in the system, the copper system was subdivided into simpler steps: from the copper (II) oxide till the pure metallic copper powder. The copper oxides indeed showed a simple mechanism of reaction, while the analysis of the pure copper powder showed that the overlap of many reactions make difficult the full comprehension of the kinetics of the mechanism involved.

As it can be seen from the plot below the behavior of the copper cube samples is much more complex, and sometimes is even experiment dependent.
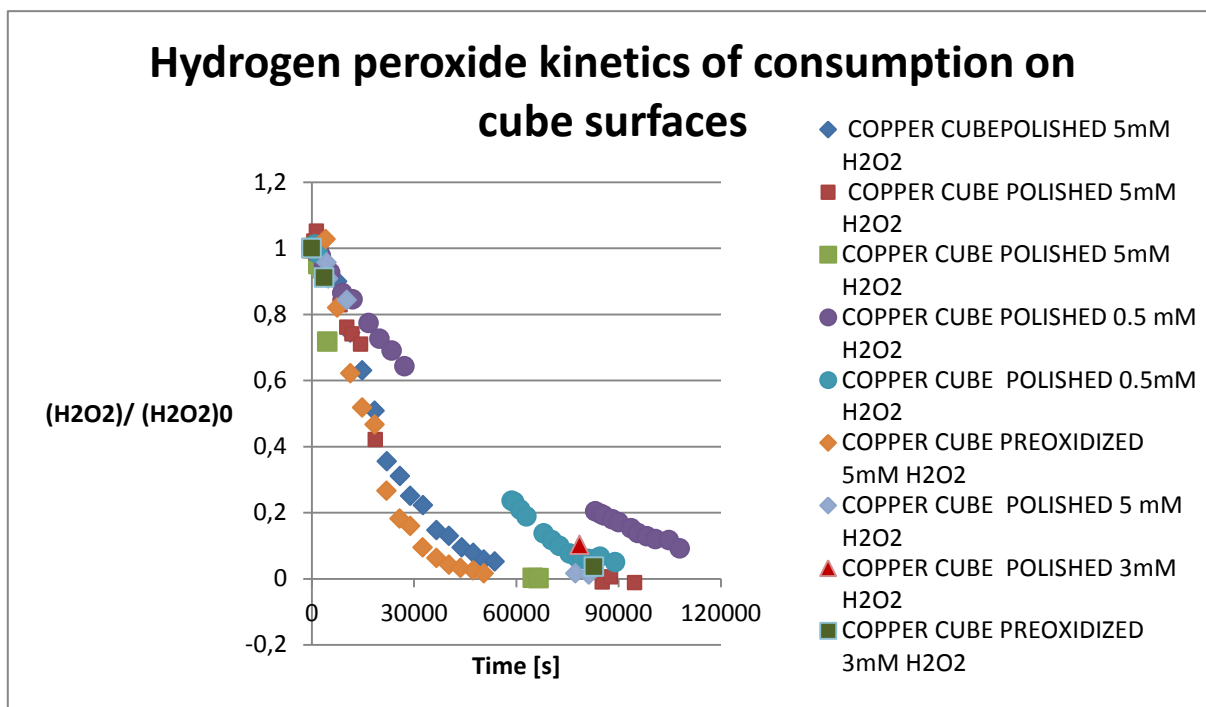
Figure 7.8 Normalized concentration of H_2O_2 (experiments at 5mM, 3mM and 0.5mM) as a function of reaction time for the reaction with copper cube polished and preoxidized samples

The trend of consumption of hydrogen peroxide in figure 7.8 shows that at equal surface area to volume ratio of copper, at higher concentration of H_2O_2 the rate of consumption is faster. The kinetics of consumption of hydrogen peroxide is much slower in cubes exposed to a lower value of H_2O_2 (see experiments at 0.5 mM). The amount of hydrogen peroxide in solution also affects the amount of copper releases in solution, from the ICP results of the previous chapter is evident that the releases of copper were ten times higher in the system with 5mM of H_2O_2 respect to the 0.5mM one.

The kinetics of consumption of hydrogen peroxide has a clear trend regarding the rate of consumption related to the amount of hydrogen peroxide.

Some experiments performed with cube samples that were preoxidized show that the preoxidation can either affect the kinetics with the consequence increase of rate of decomposition or affect the surface with a layer of stable oxide which protects the surface from further oxide attacks.

The kinetics of decomposition of hydrogen peroxide of the two overnight cubes experiments are analyzed here with the logarithmic analysis. The assumption of the first order kinetics is an approximation, the fit of the experimental data is not well described by the straight line but still this analysis allows the comparison of the two cases, see figure 7.9.
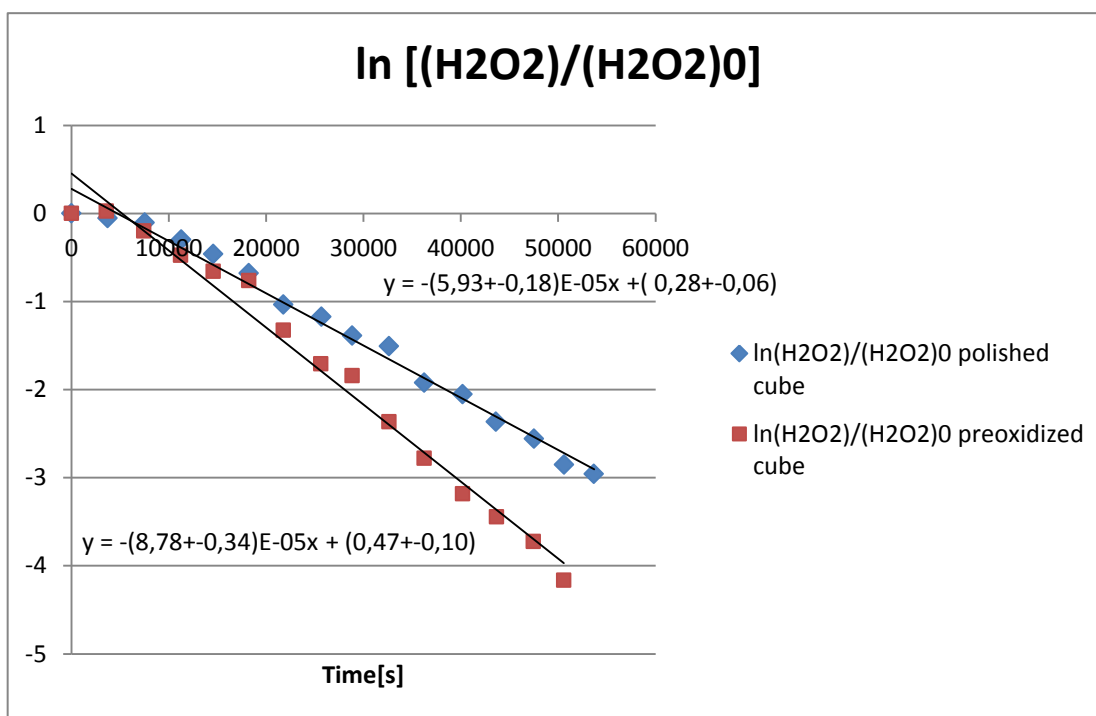
Figure 7.9 Depiction of $\ln[(H_2O_2)/(H_2O_2)_0]$ as a function of reaction time for copper cube overnight experiment 26 June.

From the logarithmic analysis is evident that the preoxidized cube has a higher pseudo first order rate constant, $k_1=(8,78\pm0,34)\cdot10^{-5}$ s^{-1}, than the polished cube, $k_1=(5,93\pm0,18)\cdot10^{-5}$ s^{-1}. The difference between the two experiments is slightly different, but the trend of consumption is faster for the cube which was treated with hydrogen peroxide before the experiment.

The same behavior is reported for the experiment performed with the so called copper cube (1) and (2) where the polished cube has a slower rate of consumption of hydrogen peroxide compared to the one preoxidized. The trend can be seen in figure 7.8, in this case the solution was at a different concentration of hydrogen peroxidized, so that 3mM.

As already said the preoxidation makes the surface of the copper cube more subject to further oxidative processes, this was also previously demonstrated in chapter 6 were the preoxidized cube shows a much corroded surface in SEM images.

The role of the oxide layer on the surface of the polished pure copper is not totally explained, in some experiments was found that the oxide layer did not affect the stability of the surface but instead gave a total protection against oxidative processes.

The role of the oxide layer has to be investigated much in deep, as it is also needed to be better understood the role of the hydroxyl radicals in the system.

The figure 7.10 shows all the experimental data of formaldehyde concentrations gained in experiments with copper cubes exposed to various concentration of hydrogen peroxide at different conditions.
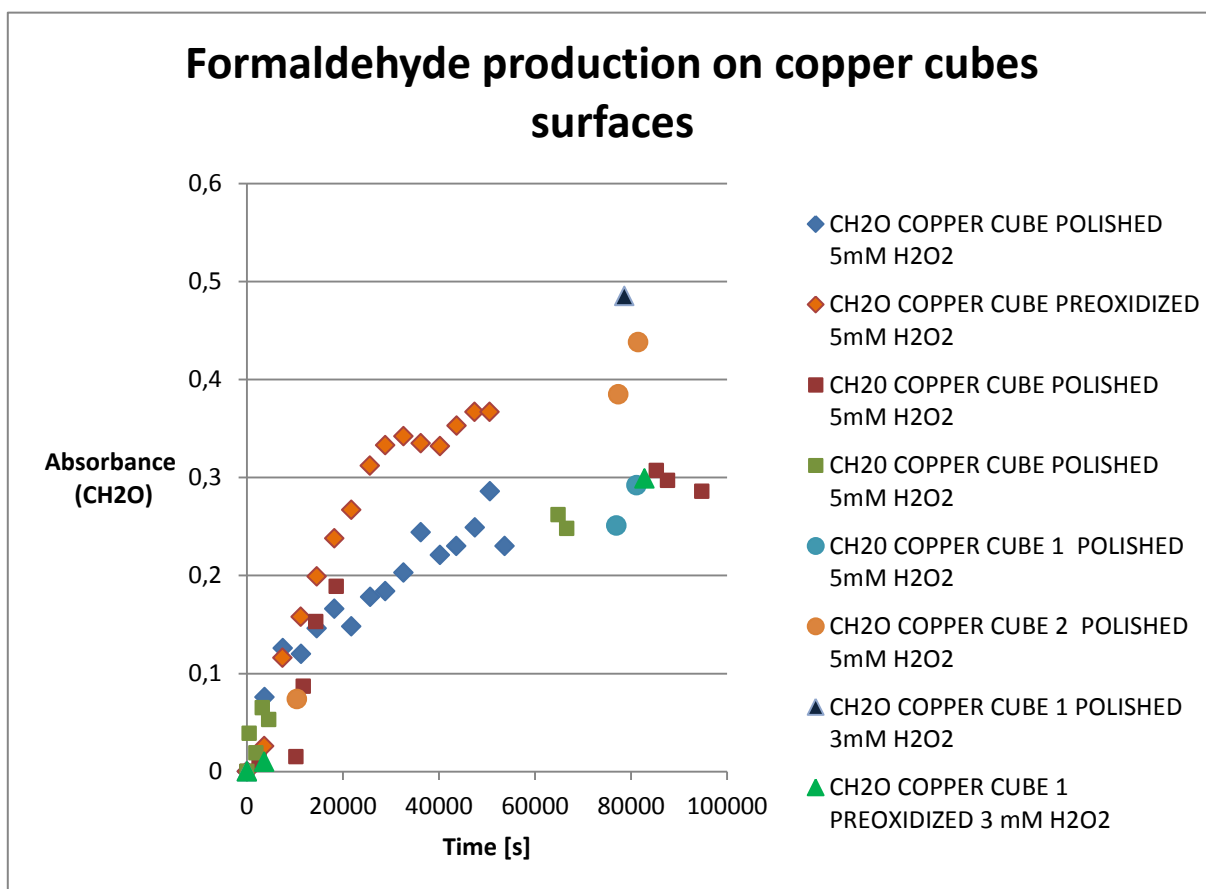
Figure 7.10 Absorbance of formaldehyde (experiments at 5mM and 3mM of H_2O_2) as a function of reaction time for copper cube polished and preoxidized samples

The trend of formaldehyde production, that is related to hydroxyl radicals in the system, is various for the different experiments. There is no a clear behavior, it was supposed that for preoxidized surfaces the production of formaldehyde was higher than for polished ones. But in some experiments this trend was the opposite, indeed in polished cube experiments the production of formaldehyde was much higher than in the same experiment conditions involving the preoxidized cube (1) and (2).

The analysis of production of formaldehyde and the role of hydroxyl radicals need to be studied in more detail with further experiments at different conditions in order to better understand the role of hydroxyl radical in the oxidative processes of copper surface.

7.2 Experimental kinetics results

In this chapter were presented all the results gained in the long experimental session performed with various materials as copper oxide powders, copper powder and copper cube samples.

The purpose of analyzing the copper oxides is to simplify the complex system of copper metallic surface in contact with hydrogen peroxide: investigating first the oxides make possible to understand the different steps of the mechanism of corrosion of copper due to hydrogen peroxide in anoxic conditions.

The copper oxides analysis brought few important results regarding the assumption of the mechanism of reaction involving hydrogen peroxide and hydroxyl radicals.

The cuprite system has a higher level of complexity with respect to the tenorite one, this is due to the fact that there are more reactions involving the powder of copper (I) oxide in contact with hydrogen peroxide with respect to the copper powder at highest level of oxidation, namely the tenorite powder.

From the tenorite experimental analysis it was demonstrated that the most common reaction that takes place between the copper (II) oxide surface and the hydrogen peroxide is the catalytic decomposition, this reaction produces basically HO·. Indeed in tenorite experiments large amounts of formaldehyde are formed and detected, this is due to the fact that the catalytic decomposition reaction is much faster than the adsorption of H_2O_2 on the surface. The kinetics of the reaction can be approached as a first order kinetics, the system is indeed quite simple.

The system considering the cuprite is indeed much complex, others reactions take place in the system in which the powder is at the first level of oxidation and so that can be involved in further processes of oxidation. The Cu(I) in contact with a molecule of H_2O_2 can be oxidized towards Cu(II) in a surface reaction, but it can also take part to the so called "Fenton – like" reaction in solution. The competition of these reactions increases the complexity of the system. Besides the catalytic decomposition on copper (II) oxide there are also the homogeneous reaction in solution of Cu(I) reacting with H_2O_2 and the surface reaction on copper (I) oxide.

The increased number of reactions that take place in the system, which enhance the complexity of the system, reflects the complexity of experimental data which are no longer approximated via a first order analysis. The cuprite system reveals indeed a much complex behavior of formaldehyde data produced in the system, while for both powders the trend of consumption of hydrogen peroxide follows the same behavior with respect to the amount of powder.

The copper powder experiments showed an increase of complexity of the system, the reason can be explained with the fact that all the reactions occurring in the cuprite system are present plus others reactions involving the oxidative processes of pure copper.

All the analysis were necessary to clarify some aspects occurring in the copper cube samples experiments.

The copper cube samples exposed to the hydrogen peroxide solution were analyzed in order to understand if the presence of hydrogen peroxide in an aqueous anoxic environment could

affect the stability of the copper canister surface which is required to be stable and inert from corrosion processes.

Even if it is not fully understood the influence of H_2O_2 and $HO\cdot$ on the pure metallic surface, it has been demonstrated that the presence of these oxidant species corrode the surface of the copper. The influence of the oxide layer on the pure metallic surface can affect the stability of copper provoking serious damages on the surface, or on the contrary could be able to stabilize the system and protect it from further attacks.

Many others analysis are necessary in order to better understand the processes of radiation induced corrosion of copper. The purpose is to validate or not the assumption of inactivity of copper in contact with water in anoxic conditions.

Conclusions

In this work it has been demonstrated that the copper surface of KBS − 3 canisters used as main barrier against radioactive releases is not inert towards the species produced during the radiolysis of water due to irradiation.

The corrosive processes involving the copper surface were analyzed through irradiation and hydrogen peroxide experiments on different copper samples.

The kinetics results of copper powder and copper oxides powder experiments demonstrated the influence of the catalytic decomposition of hydrogen peroxide on the surface of copper oxide.

Thanks to kinetics analysis performed on copper (II) oxide it was demonstrated that the main reaction of decomposition of hydrogen peroxide is the catalytic decomposition. The production of hydroxyl radical from this reaction is significant but the influence of this radical on the corrosion driven processes is not yet well evaluated so further experiments need to be performed.

The experiments performed with copper (I) oxide showed that besides the reaction of decomposition of hydrogen peroxide on the surface other processes are involved, one of them is the homogeneous reaction of Cu(I) in solution.

The copper powder experimental analysis gave relevant suggestions about the implementation of the detection methods for hydrogen peroxide and hydroxyl radical. The reactions occurring on this material are several and are in agreement with the reactions evaluated for the oxides.

The experiments performed with copper canister samples reveal the impact of aqueous radiolysis chemistry on the process of radiation induced corrosion of copper.

The results of all experiments show that the corrosion processes are mainly due to the presence of hydrogen peroxide in the anoxic water.

The linear dependence between copper releases in solution and concentration of hydrogen peroxide is demonstrated from analysis at ICP. The molecule of hydrogen peroxide is decomposed on the copper oxide surface and the result of this reaction is the formation of an oxide layer that can be further corroded by the products of the catalytic decomposition of this oxidant.

The SEM analysis on the cubic copper surfaces showed the characteristic features of radiation enhanced corrosion.

The surfaces exposed to hydrogen peroxide present the same corrosion features evaluated in samples exposed to irradiation. The combination of irradiation and exposition to hydrogen peroxide in some experiments showed an enhancement in the copper releases in solution, this result points out the crucial role of this species in the radiation induced corrosion processes.

The formation of the oxide layer on the surface of the samples was demonstrated to have a crucial role in the corrosion resistance properties referred to copper.

During a copper sample experiment, an inert behavior of its surface in contact with hydrogen peroxide is interpreted as due to the formation of a homogeneous oxide layer. The formation of a homogeneous oxide layer on its surface developed an unexpected corrosion resistance property that requires further investigations and experimental confirmations.

Future works

The results achieved during the experimental session revealed some suggestions for the development of new experiments.

The investigation of the role of the copper oxide layer in the radiation enhanced corrosion need to be studied in deep. Many other experiments of copper samples exposed to irradiation and hydrogen peroxide solutions at different concentrations need to be developed.

In order to clarify the properties of a homogeneous oxide layer on the copper surface, an experiment involving some copper cube samples stored in a humid controlled atmosphere is planned. The purpose of this experiment consists in the exposure of samples to the experimental hydrogen peroxide solution after the formation of the homogeneous oxide layer on their surface. The results from this experiment are supposed to show the same behavior obtained from the inert copper cube sample previously reported. The analysis with SEM for the characterization of the surfaces of these samples is required.

During this work was carried out an experiment involving a copper powder sample exposed to irradiation with the gamma source. The sample of copper powder was stored in a reactor vessel containing the same solution used in hydrogen peroxide experiments, but without the hydrogen peroxide. The sample was exposed to a total dose that simulates the production of hydrogen peroxide usually inserted in the reactant solution. During the experiment many samples were taken and the kinetics of consumption of hydrogen peroxide and formation of hydroxyl radical were evaluated with the Ghormley and Modified Hantzsch methods.

The implementation of this kind of experiments is quite complicated, but it would be really interesting to perform various experiments involving the copper powder, the copper oxide and the copper cube samples.

One of the main purpose of this irradiation experiment is to understand the behavior of the hydroxyl radical in contact with copper. The comparison of experiments performed with and without the sample inserted in the reaction vessel would underline the reactivity of the hydroxyl radical towards the surface of copper. The detection of the hydroxyl radical in the system should be the same in both experiments if the hydroxyl radical would have no reactivity towards the surface of the material, because only the radicals produced by water radiolysis should be produced in the reactant solution.

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