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# Optimization of the $\text{CeO}_2/\text{CeCl}_3$ cycle by cerium IV oxide reductive dissolution catalysis

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## ABSTRACT

While thermochemical cycles can be a way to produce hydrogen, physiochemical studies show that implementing them is often difficult for reactivity reasons. Most of the cycles actually involve solid–gas type systems with limited reactivity due to interface passivation processes. To overcome this difficulty, studies have shown that using the  $\text{CeO}_2/\text{CeCl}_3$  pair, in which the cerium undergoes a reversible oxidation–reduction cycle, has enormous potential since it may partially be carried out in aqueous phase by reductive dissolution from cerium oxides (IV) to cerium chloride (III).

If the first reaction of the cycle is well known for industrial application, its second and its third reaction still need some investigation. Thus, this article primarily describes the work done on the second reaction to assess the possibility of carrying out cerium reduction in aqueous phase. The extremely positive results have highlighted the possibility of achieving 100% reaction efficiency in systems catalyzed by fluoride ions. Conducting the reaction with in-line distillation of the excess water also helps significantly reduce reaction time which offers good potential for the next stage. A ratio of 8 ml of a 20 w% HCl solution per gram of  $\text{CeO}_2$  containing 6w% of  $\text{CaF}_2$  leads to ensure a total reaction in a few minutes at 108.6 °C (boiling temperature of the  $\text{H}_2\text{O}$ –HCl azeotrope).

The work presented herein also describes a brief feasibility study for the third reaction cycle which could be carried out by spraying the solution from the second reaction, in a hot column whose temperature will be determined by further work. These results have allowed upgrading the first flowsheet proposed in a previous publication.

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## Introduction

Hydrogen can be produced in various ways depending on the choice of the primary energy source. Thermochemical cycles combined with heat sources may be a sensible choice since this avoids the energy breakdown caused by power generation, as is the case for example in electrolytic treatment which

uses power [1]. Studies conducted in the field of cycles have shown that many of them implement solid–gas systems and therefore are unlikely to bear fruit for reasons of reactivity. The passivating layers created on the surface of reagents limits progress and reaction kinetics which means having to oversize installations which, at the outset, are already sizeable.

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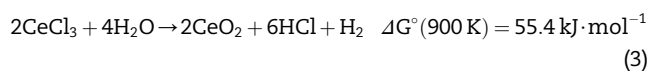
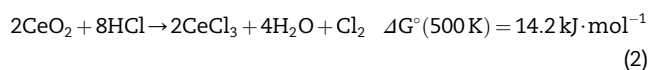
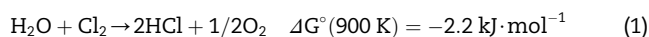
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To overcome this difficulty, research has been conducted to try to identify a cycle that would allow total or partial burnup of reagents and minimize the quantities of material involved while, at the same time, optimizing reaction kinetics. This was how the chlorine–cerium cycle previously studied under dry way [2], was identified as a likely candidate because its architecture would enable carrying out one of its stages in aqueous state to fully dissolve cerium chloride and avoid passivation of CeO<sub>2</sub> particles by deposits of CeCl<sub>3</sub> [3]. Experimental tests on the subject showed good feasibility of chlorination and hydrolysis reactions: they also showed that the chlorination reaction should be conducted under certain conditions so as to have acceptable kinetics. The presence of fluorine does seem essential to ensure optimal reaction progress in a time frame that is compatible with industrial use.

### CeO<sub>2</sub>–CeCl<sub>3</sub> cycle

The thermochemical cycle, based on the use of cerium, has three steps whose sequence is as follows:



- The first reaction is the opposite of what is commonly called the Deacon reaction widely used in industry to produce chlorine. The reverse Deacon reaction, which has been the subject of many studies conducted in the context of hydrogen production, should be carried out at around 600 °C; temperature at which kinetic parameters have been studied [4] without using a catalyst. A proposal for an industrial application shows that this reaction can be catalyzed by passing the shielding gas through a solid catalyst bed to bring its operating temperature to around 100 °C [5]. A third way, not yet studied and which could avoid the use of a solid catalyst imposing kinetics limited to gas–solid surface reactions, would be to implement light radiation. Chlorine easily forms radicals under UV radiation at wavelengths between 250 and 450 nm with optimal efficiency at 335 nm [6].
- The second reaction has been the subject of a study detailed in a previous paper [3]. This study concluded a distinct advantage in conducting it in aqueous phase by reductive dissolution of CeO<sub>2</sub> in a hydrochloric acid solution having a concentration close to that of the gaseous azeotrope. A continuous distillation of the water formed, conveyed to the third reaction keeps the concentration of HCl at an optimal level and therefore maintains dissolution kinetics. Dissolution in turn ensures burnup of the CeO<sub>2</sub> reagent which will be regenerated during the third reaction. Experimental tests carried out using this mode have

demonstrated the need for a catalyst which will be detailed in this publication.

- The third and most endothermic reaction may, according to the system proposed for implementing the second reaction, take place between the solvent H<sub>2</sub>O and solute CeCl<sub>3</sub> generated during the second reaction. By “instantly” volatilizing the solution, a rapid and complete gas–gas type reaction may occur. This article proposes an implementation protocol for this hydrolysis reaction and provides the first experimental results.

## Hydrochlorination reaction and reactivity of CeO<sub>2</sub>

### Advantage of fluorine

It was found, in the hydrochlorination tests described in a previous publication [3], that the reactivity of cerium oxide depends on the powder lot used, whose color varies between yellow and white. Four different lots from Acros and Alfa suppliers were tested after having been ground in a PM4000 ball mill at 150 rpm for 75 min. The specific surface areas of each powder obtained were measured using the BET method. The tests consisted of putting 10 g of CeO<sub>2</sub> from each lot in a flask containing a cold, stirred, 36% HCl solution. The duration of each test was 4 h. Only one sample showed a strong reaction according to the qualitative results presented in Table 1.

A comparative XRD analysis performed on the four lots identified the presence of a very small fraction of cerium fluoride in lot A as shown in the Fig. 1 spectrum. Lots B, C and D on the other hand only showed the CeO<sub>2</sub> diffraction pattern.

These traces of fluoride, not indicated on the product packaging may come from bastnasite constituting the carbonate ore from which cerium [7] is mined and contains a variable proportion of fluoride. To date, no publication appears to give any role whatsoever to fluoride in the cerium oxide dissolution process in hydrochloric acid.

### Experimental study of the hydrochlorination reaction

According to the second cycle reaction (2), the reaction progress is defined by the ratio between the initial quantity of CeO<sub>2</sub> and the quantity of formed CeCl<sub>3</sub>. This quantity is equal to the quantity of Cl<sub>2</sub> released that can be monitored thanks to a chlorine analysis unit.

$$\text{Reaction progress} = \frac{2n_{\text{Cl}_2}}{(n_{\text{CeO}_2})_0} \quad (4)$$

**Table 1 – Reactivity of different lots of CeO<sub>2</sub> powder.**

Lot no.	Source	Color	Specific surface m <sup>2</sup> /g	Reaction progress
A	Acros	White	0.19	100%
B	Acros	Light yellow	1.98	0%
C	Alfa	Light yellow	4.52	0%
D	Alfa	White	4.34	~5%

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