International Journal of Hydrogen Energy, Vol. 1, pp. 23–32. Pergamon Press, 1976. Printed in Northern Ireland

A THERMOCHEMICAL PROCESS FOR HYDROGEN PRODUCTION

K. F. Knoche, H. Cremer and G. Steinborn

Lehrstuhl für Technische Thermodynamik, Technische Hochschule Aachen, West Germany

Abstract—A thermochemical water splitting process of the iron–chlorine family is presented and the mass and energy flows of this process are discussed in detail. This proposal represents one alternative of a great variety of closed thermochemical processes of the iron–chlorine family.

THE IRON–CHLORINE FAMILY

Water splitting processes of the iron–chlorine family, operating with iron-oxides, iron-chlorides, chlorine and hydrochloric acid, seem to be rather promising for future hydrogen production. All the chemical reactions involved in processes of this type are quick enough for technical application with adequate yield of the desired products. Even the thermal decomposition of iron (III)–chloride to iron (II)–chloride and chlorine—which has an equilibrium chlorine yield of only 10% under favourable conditions—can be performed with sufficient yields when operated in a so-called hot–cold apparatus (cf. below).

Iron–chlorine reactions have been investigated quite intensively during the last 20 years, hence the chemistry and the thermodynamics of these reactions are quite wellknown; a literature survey has been reported [1].†

From 56 reactions which have been computed [2, 3], more than 350 closed cycles could be compiled. Though these 56 reaction equations are meaningful from thermodynamic aspects, they still include a number of equations which are not suitable with respect to chemical engineering. Those equations have been cancelled using the following criteria:

- no oxidation with oxygen;
- no reaction between oxides and chlorides;
- no reduction of oxides with hydrogen;
- no reduction of iron (III)-chloride with hydrogen;
- no hydrolysis of iron (III)-chloride;
- no hydrolysis of a mixture of iron and iron (III)-chloride;
- no hydrolysis of iron (II)-chloride with additional chlorine;
- not more than one hydrolysis reaction of iron (II)-chloride;
- no reactions including ironoxychlorides;
- not more than 2 chlorinating reactions in a cycle or 2 chlorinations with the same chlorinating agent.

Following these criteria the essential reactions being involved in iron–chlorine cycles can be concentrated to five typical groups:

(1) Hydrolysis of either iron, iron (II)-oxide or iron (II)-chloride;
(2) Chlorination of iron oxide with chlorine or hydrochloric acid or a mixture of both;
(3) Thermal decomposition of iron (III)-chloride to iron (II)-chloride;
(4) Regeneration of the chlorinating agent (either chlorine or hydrochloric acid);
(5) Possibly a reduction step.

Table 1 shows typical reactants and products of these groups as well as the chemical reactions, the temperature range, the optimum temperature (with respect to yield) and the heat requirements at optimum temperature. The five groups of reactions contain 18 reaction equations which can be combined to 35 multi-step processes of the iron–chlorine family listed in Table 2.

The great number of possible variations in the sequence of chemical reactions result in many

† This publication summarizes as well the experimental activities in the field which have been done at the Joint Nuclear Research Center, Ispra, Italy and at the authors institute.

TABLE 1. Typical reactions in iron–chlorine processes

Typical groups	Reactants: solid	Reactants: gaseous	Products: solid	Products: gaseous	Chemical Reaction	Temperature range K	opt. Temp. K	ΔH reakt at opt. Temp. kJ/mol
Chlorination	FeO	Cl_2	-	$FeCl_3$, O_2, Cl_2	$FeO + 3/2\ Cl_2 = FeCl_3 + 1/2\ O_2$	1000-1300	1100	+ 9.004
	Fe_3O_4		Fe_2O_3	$FeCl_3$, Cl_2	$Fe_3O_4 + 1/2\ Cl_2 = 1/3FeCl_3 + 4/3Fe_2O_3$	700-1300	1300	- 71.242
			-	$FeCl_3$, O_2, Cl_2	$Fe_3O_4 + 9/2\ Cl_2 = 3FeCl_3 + 2\ O_2$	1100-1300	1300	+ 301.733
	Fe_2O_3				$Fe_2O_3 + 3\ Cl_2 = 2FeCl_3 + 3/2\ O_2$	1100-1300	1300	+ 279.935
	Fe_3O_4	HCl	$FeCl_2$	Cl_2, H_2O, HCl	$Fe_3O_4 + 8HCl = 3FeCl_2 + Cl_2 + 4H_2O$	400- 750	500	-138.026
				Fe_2Cl_6, H_2O, HCl	$Fe_3O_4 + 8HCl = FeCl_2 + Fe_2Cl_6 + 4H_2O$	300 -700	650	-112.413
	Fe_2O_3		-		$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O$	300- 700	700	- 10.701
	Fe_3O_4	Cl_2, HCl	-	Fe_2Cl_6, H_2O, HCl, Cl_2	$Fe_3O_4 + 1/2\ Cl_2 + 8HCl = 3/2\ Fe_2Cl_6 + 4H_2O$	600-1100	700	- 107.775
Hydrolysis	Fe	H_2O	FeO	H_2 , H_2O	$Fe + H_2O = FeO + H_2$	600-1300	600	- 24.086
			Fe_3O_4		$3Fe + 4H_2O = Fe_3O_4 + 4H_2$	800-1300	600	- 127.379
	FeO				$3FeO + H_2O = Fe_3O_4 + H_2$	800-1300	600	- 55.096
	$FeCl_2$		FeO	H_2O, HCl	$FeCl_2 + H_2O = FeO + 2HCl$	900-1300	1200	+ 76.432
			Fe_3O_4	H_2, H_2O, HCl	$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2$	900-1300	1200	+ 194.750
Thermal decomposition	-	Fe_2Cl_6	$FeCl_2$	Fe_2Cl_2, Cl_2	$Fe_2Cl_6 = Cl_2 + 2FeCl_2$	577-700	600	- 24.689
Regeneration of chlorinating agent	-	HCl, O_2	-	Cl_2, HCl, O_2, H_2O	$2HCl + 1/2\ O_2 = Cl_2 + H_2O$	400-800	700	- 59.129
		Cl_2, H_2O			$Cl_2 + H_2O = 2HCl + 1/2\ O_2$	1000-1300	1300	+ 60.265
	Fe_3O_4		Fe_2O_3	HCl, H_2O, Cl_2	$1/2\ Cl_2 + Fe_3O_4 + 1/2H_2O = 3/2Fe_2O_3 + HCl$	400-1300	1300	- 88.036
Reduction	-	$FeCl_2$, H_2	Fe	HCl, H_2, $FeCl_2$	$FeCl_2 + H_2 = Fe + 2HCl$	1000-1300	1150	+ 100.901

TABLE 2. Thermochemical water splitting processes of the iron–chlorine family

(1)	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$Fe_3O_4 + 8HCl$	=	$Cl_2 + 3FeCl_2 + 4H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(2)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/2\ Cl_2 + Fe_3O_4$	=	$3FeCl_3 + 2O_2$
	$6HCl\ 8\ 3/2\ O_2$	=	$3Cl_2 + 3H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(3)	$3/4\ FeCl_3$	=	$3/8\ Cl_2 + 3/4\ FeCl_2$
	$9/8\ Cl_2 + 1/4\ Fe_3O_4$	=	$3/4\ FeCl_3 + 1/2\ O_2$
	$3/4\ Fe_3O_4 + 6HCl$	=	$3/4\ Cl_2 + 9/4\ FeCl_2 + 3H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(4)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/8\ Cl_2 + 1/4\ Fe_3O_4$	=	$3/4\ FeCl_3 + 1/2\ O_2$
	$3/8\ Cl_2 + 6HCl + 3/4\ Fe_3O_4$	=	$9/4\ FeCl_3 + 3H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(5)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$1/2\ Cl_2 + Fe_3O_4 + 8HCl$	=	$3FeCl_3 + 4H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(6)	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$3FeCl_2 + 3H_2$	=	$3Fe + 6HCl$
	$3Fe + 4H_2O$	=	$Fe_3O_4 + 4H_2$
	$Fe_3O_4 + 8HCl$	=	$Cl_2 + 3FeCl_2 + 4H_2O$
(7)	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$3FeCl_2 + 3H_2O$	=	$3FeO + 6HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$Fe_3O_4 + 8HCl$	=	$Cl_2 + 3FeCl_2 + 4H_2O$
(8)	$FeCl_3$	=	$1/2\ Cl_2 + FeCl_2$
	$3/2\ Cl_2 + FeO$	=	$FeCl_3 + 1/2\ O_2$
	$4FeCl_2 + 4H_2O$	=	$4FeO + 8HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$Fe_3O_4 + 8HCl$	=	$Cl_2 + 3FeCl_2 + 4H_2O$
(9)	$4FeCl_3$	=	$2Cl_2 + 4FeCl_2$
	$3/2\ Cl_2 + FeO$	=	$FeCl_3 + 1/2\ O_2$
	$4FeCl_2 + 4H_2O$	=	$4FeO + 8HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$1/2\ Cl_2 + Fe_3O_4 + 8HCl$	=	$3FeCl_3 + 4H_2O$
(10)	$FeCl_3$	=	$1/2\ Cl_2 + FeCl_2$
	$3/2\ Cl_2 + FeO$	=	$FeCl_3 + 1/2\ O_2$
	$FeCl_2 + H_2O$	=	$FeO + 2HCl$
	$Fe_3O_4 + 8HCl$	=	$Cl_2 + 3FeCl_2 + 4H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(11)	$4FeCl_3$	=	$2Cl_2 + 4FeCl_2$
	$3/2\ Cl_2 + FeO$	=	$FeCl_3 + 1/2\ O_2$
	$FeCl_2 + H_2O$	=	$FeO + 2HCl$
	$1/2\ Cl_2 + Fe_3O_4 + 8HCl$	=	$3FeCl_3 + 4H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$

TABLE 2. (continued)

(12)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/2\ Cl_2 + Fe_3O_4$	=	$3FeCl_3 + 2O_2$
	$6HCl + 3/2\ O_2$	=	$3Cl_2 + 3H_2O$
	$3FeCl_2 + 3H_2$	=	$3Fe + 6HCl$
	$3Fe + 4H_2O$	=	$Fe_3O_4 + 4H_2$
(13)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/2\ Cl_2 + Fe_3O_4$	=	$3FeCl_3 + 2O_2$
	$6HCl + 3/2\ O_2$	=	$3Cl_2 + 3H_2O$
	$3FeCl_2 + 3H_2O$	=	$3FeO + 6HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
(14)	$3/4\ FeCl_3$	=	$3/8\ Cl_2 + 3/4\ FeCl_2$
	$9/8\ Cl_2 + 1/4\ Fe_3O_4$	=	$3/4\ FeCl_3 + 1/2\ O_2$
	$3FeCl_2 + 3H_2$	=	$3Fe + 6HCl$
	$3Fe + 4H_2O$	=	$Fe_3O_4 + 4H_2$
	$3/4\ Fe_3O_4 + 6HCl$	=	$3/4\ Cl_2 + 9/4\ FeCl_2 + 3H_2O$
(15)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/8\ Cl_2 + 1/4\ Fe_3O_4$	=	$3/4\ FeCl_3 + 1/2\ O_2$
	$3FeCl_2 + 3H_2$	=	$3Fe + 6HCl$
	$3Fe + 4H_2O$	=	$Fe_3O_4 + 4H_2$
	$3/8\ Cl_2 + 3/4\ Fe_3O_4 + 6HCl$	=	$9/4\ FeCl_3 + 3H_2O$
(16)	$3/4\ FeCl_3$	=	$3/8\ Cl_2 + 3/4\ FeCl_2$
	$9/8\ Cl_2 + 1/4\ Fe_3O_4$	=	$3/4\ FeCl_3 + 1/2\ O_2$
	$3FeCl_2 + 3H_2O$	=	$3FeO + 6HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$3/4\ Fe_3O_4 + 6HCl$	=	$3/4\ Cl_2 + 9/4\ FeCl_2 + 3H_2O$
(17)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/8\ Cl_2 + 1/4\ Fe_3O_4$	=	$3/4\ FeCl_3 + 1/2\ O_2$
	$3FeCl_2 + 3H_2O$	=	$3FeO + 6HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$3/8\ Cl_2 + 3/4\ Fe_3O_4 + 6HCl$	=	$9/4\ FeCl_3 + 3H_2O$
(18)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$3FeCl_2 + 3H_2$	=	$3Fe + 6HCl$
	$3Fe + 4H_2O$	=	$Fe_3O_4 + 4H_2$
	$1/2\ Cl_2 + Fe_3O_4 + 8HCl$	=	$3FeCl_3 + 4H_2O$
(19)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$3FeCl_2 + 3H_2O$	=	$3FeO + 6HCl$
	$3FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$1/2\ Cl_2 + Fe_3O_4 + 8HCl$	=	$3FeCl_3 + 4H_2O$
(20)	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$3FeCl_2 + 3H_2$	=	$3Fe + 6HCl$
	$3Fe + 3H_2O$	=	$3FeO + 3H_2$
	$4FeO + H_2O$	=	$Fe_3O_4 + H_2$
	$Fe_3O_4 + 8HCl$	=	$Cl_2 + 3FeCl_2 + 4H_2O$
(21)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$1/2\ Cl_2 + Fe_3O_4$	=	$1/3\ FeCl_3 + 4/3\ Fe_2O_3$
	$Cl_2 + H_2O$	=	$2HCl + 1/2\ O_2$
	$4/3\ Fe_2O_3 + 8HCl$	=	$8/3\ FeCl_3 + 4H_2O$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(22)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$9/2\ Cl_2 + 3/2\ Fe_2O_3$	=	$3FeCl_3 + 9/4\ O_2$
	$7HCl + 7/4\ O_2$	=	$7/2\ Cl_2 + 7/2\ H_2O$
	$1/2\ Cl_2 + Fe_3O_4 + 1/2\ H_2O$	=	$3/2\ Fe_2O_3 + HCl$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$
(23)	$3FeCl_3$	=	$3/2\ Cl_2 + 3FeCl_2$
	$Cl_2 + 1/3\ Fe_2O_3$	=	$2/3\ FeCl_3 + 3/2\ O_2$
	$7/6\ Fe_2O_3 + 7HCl$	=	$7/3\ FeCl_3 + 21/6\ H_2O$
	$1/2\ Cl_2 + Fe_3O_4 + 1/2\ H_2O$	=	$3/2\ Fe_2O_3 + HCl$
	$3FeCl_2 + 4H_2O$	=	$Fe_3O_4 + 6HCl + H_2$

TABLE 2. (continued)

(24)	$2/3\,FeCl_3$	$= 1/3\,Cl_2 + 2/3\,FeCl_2$
	$Cl_2 + 1/3\,Fe_2O_3$	$= 2/3\,FeCl_3 + 1/2\,O_2$
	$7/9\,Fe_3O_4 + 56/9\,HCl$	$= 7/9\,Cl_2 + 21/9\,FeCl_2 + 28/9\,H_2O$
	$1/9\,Cl_2 + 2/9\,Fe_3O_4 + 1/9\,H_2O$	$= 1/3\,Fe_2O_3 + 2/9\,HCl$
	$3FeCl_2 + 4H_2O$	$= Fe_3O_4 + 6HCl + H_2$
(25)	$3FeCl_3$	$= 3/2\,Cl_2 + 3FeCl_2$
	$Cl_2 + 1/3\,Fe_2O_3$	$= 2/3\,FeCl_3 + 1/2\,O_2$
	$7/18\,Cl_2 + 7/9\,Fe_3O_4 + 56/9\,HCl$	$= 7/3\,FeCl_3 + 28/9\,H_2O$
	$1/9\,Cl_2 + 2/9\,Fe_3O_4 + 1/9\,H_2O$	$= 1/3Fe_2O_3 + 2/9\,HCl$
	$3FeCl_2 + 4H_2O$	$= Fe_3O_4 + 6HCl + H_2$
(26)	$20/9\,FeCl_3$	$= 10/9\,Cl_2 + 20/9\,FeCl_2$
	$Cl_2 + 1/3\,Fe_2O_3$	$= 2/3\,FeCl_3 + 1/2\,O_2$
	$1/9\,Cl_2 + 2/9\,Fe_3O_4 + 1/9\,H_2O$	$= 1/3\,Fe_2O_3 + 2/9\,HCl$
	$7/9\,Fe_3O_4 + 56/9\,HCl$	$= 7/9\,FeCl_2 + 14/9\,FeCl_3 + 28/9\,H_2O$
(27)	$9/4\,FeCl_3$	$= 9/8\,Cl_2 + 9/4\,FeCl_2$
	$9/8\,Cl_2 + 1/4\,Fe_3O_4$	$= 3/4\,FeCl_3 + 1/2\,O_2$
	$3FeCl_2 + 3H_2$	$= 3Fe + 6HCl$
	$3Fe + 4H_2O$	$= Fe_3O_4 + 4H_2$
	$3/4\,Fe_3O_4 + 6HCl$	$= 3/4\,FeCl_2 + 3/2\,FeCl_3 + 3H_2O$
(28)	$9/4\,FeCl_3$	$= 9/8\,Cl_2 + 9/4\,FeCl_2$
	$9/8\,Cl_2 + 1/4\,Fe_3O_4$	$= 3/4\,FeCl_3 + 1/2\,O_2$
	$3/4\,Fe_3O_4 + 6HCl$	$= 3/4\,FeCl_2 + 3/2\,FeCl_3 + 3H_2O$
	$3FeCl_2 + 4H_2O$	$= Fe_3O_4 + 6HCl + H_2$
(29)	$2FeCl_3$	$= Cl_2 + 2FeCl_2$
	$Cl_2 + H_2O$	$= 2HCl + 1/2\,O_2$
	$Fe_3O_4 + 8HCl$	$= FeCl_2 + 2FeCl_3 + 4H_2O$
	$3FeCl_2 + 4H_2O$	$= Fe_3O_4 + 6HCl + H_2$

(30)	$3FeCl_3$	$= 3/2\,Cl_2 + 3FeCl_2$
	$3/2\,Cl_2 + FeO$	$= FeCl_3 + 1/2\,O_2$
	$4FeCl_2 + 4H_2O$	$= 4FeO + 8HCl$
	$3FeO + H_2O$	$= Fe_3O_4 + H_2$
	$Fe_3O_4 + 8HCl$	$= FeCl_2 + 2FeCl_3 + 4H_2O$
(31)	$9/4\,FeCl_3$	$= 9/8\,Cl_2 + 9/4\,FeCl_2$
	$9/8\,Cl_2 + 1/4\,Fe_3O_4$	$= 3/4\,FeCl_3 + 1/2\,O_2$
	$3FeCl_2 + 3H_2O$	$= 3FeO + 6HCl$
	$3FeO + H_2O$	$= Fe_3O_4 + H_2$
	$3/4\,Fe_3O_4 + 6HCl$	$= 3/4\,FeCl_2 + 3/2\,FeCl_3 + 3H_2O$
(32)	$3FeCl_3$	$= 3/2\,Cl_2 + 3FeCl_2$
	$9/8\,Cl_2 + 1/4\,Fe_3O_4$	$= 3/4\,FeCl_3 + 1/2\,O_2$
	$9/8\,Fe_2O_3 + 27/4\,HCl$	$= 9/4\,FeCl_3 + 27/8\,H_2O$
	$3/8\,Cl_2 + 3/4\,Fe_3O_4 + 3/8\,H_2O$	$= 9/8\,Fe_2O_3 + 3/4\,HCl$
	$3FeCl_2 + 4H_2O$	$= Fe_3O_4 + 6HCl + H_2$
(33)	$2FeCl_3$	$= Cl_2 + 2FeCl_2$
	$Cl_2 + H_2O$	$= 2HCl + 1/2\,O_2$
	$3FeCl_2 + 3H_2$	$= 3Fe + 6HCl$
	$3Fe + 4H_2O$	$= Fe_3O_4 + 4H_2$
	$Fe_3O_4 + 8HCl$	$= FeCl_2 + 2FeCl_3 + 4H_2O$
(34)	$2FeCl_3$	$= Cl_2 + 2FeCl_2$
	$Cl_2 + H_2O$	$= 2HCl + 1/2\,O_2$
	$3FeCl_2 + 3H_2O$	$= 3FeO + 6HCl$
	$3FeO + H_2O$	$= Fe_3O_4 + H_2$
	$Fe_3O_4 + 8HCl$	$= FeCl_2 + 2FeCl_3 + 4H_2O$
(35)	$3FeCl_3$	$= 3/2\,Cl_2 + 3FeCl_2$
	$Cl_2 + H_2O$	$= 2HCl + 1/2\,O_2$
	$3/2\,Fe_2O_3 + 9HCl$	$= 3FeCl_3 + 9/2\,H_2O$
	$1/2\,Cl_2 + Fe_3O_4 + 1/2\,H_2O$	$= 3/2\,Fe_2O_3 + HCl$
	$3FeCl_2 + 4H_2O$	$= Fe_3O_4 + 6HCl + H_2$

alternatives of closed cycles which again allow for process optimization with respect to mass and energy flow and overall efficiency.

For technical realisation additional boundary conditions have to be considered, i.e.

- separation of products;
- transportation of solid, liquid and gaseous materials within the cycle;
- coupling of the primary energy source with the cycle;
- heat transfer within the cycle:

Separation of products is one of the most important steps for water splitting cycles, the energy requirements for separation can be considerable. However, for any individual step it is not necessary to separate all the products, as long as these products can be used in a subsequent step.

The coupling of the primary energy source will also influence the overall process. Considering nuclear heat from a HTGR, the coolant of the nuclear reactor will be circulated at a pressure of about 40 bar. Hence it might be meaningful to operate the chemical cycle at the same pressure level, especially whenever the desired products—hydrogen and oxygen shall be produced at high pressures. The pressure influence on the chemical reactions may completely change the operating conditions compared with a cycle at ambient pressure.

Furthermore materials problems should be kept in mind whenever processes of the iron–chlorine family are considered; but there are some indications (experience of a new hydrometallurgical process for the production of powdered iron (50,000 tons/year) from iron (II)-chloride operated in Canada) that materials problems may be overcome which occur with the handling of hydrochloric acid, chlorine and their solutions.

IRON–CHLORINE CYCLE

Figure 1 represents a proposal for a flow chart of an iron chlorine process where these problems are discussed more in detail. This cycle is operating according to the following scheme of reactions:

1 bar

$$\begin{aligned} 3FeCl_2 + 3H_2 &= 6HCl + 3Fe \\ 3Fe + 4H_2O &= Fe_3O_4 + 4H_2 \\ H_2O + Cl_2 &= 2HCl + 0.5O_2 \\ Fe_3O_4 + 8HCl + 0.5Cl_2 &= 1.5Fe_2Cl_6 + 4H_2O \\ 1.5Fe_2Cl_6 &= 3FeCl_2 + 1.5Cl_2 \end{aligned}$$

40 bar

$$\begin{aligned} 3FeCl_2 + 3H_2 &= 3Fe + 6HCl \\ 3Fe + 4H_2O &= Fe_3O_4 + 4H_2 \\ Fe_3O_4 + \tfrac{3}{2}H_2O + \tfrac{3}{2}Cl_2 &= \tfrac{3}{2}Fe_2O_3 + 3HCl + \tfrac{1}{2}O_2 \\ \tfrac{3}{2}Fe_2O_3 + 9HCl &= \tfrac{3}{2}Fe_2Cl_6 + \tfrac{9}{2}H_2O \\ \tfrac{3}{2}Fe_2Cl_6 &= 3FeCl_2 + \tfrac{3}{2}Cl_2 \end{aligned}$$

Both reaction schemes have an equal basis; the differences in equations (3) and (4) of both cycles result from appropriate alterations of reaction performance at the different pressure levels (1 bar and 40 bar). The consequences are discussed below.

Reduction of $FeCl_2$

The reduction of iron (II)-chloride with hydrogen according to the equation

$$FeCl_2 + H_2 = Fe + 2HCl$$

is most favourable at high temperatures. Hydrogen is heated by a counterflow preheater and afterwards in a heat-exchanger where the maximum process temperature of about 1300 K is reached by exchanging heat with the helium from the high temperature reactor. Excess of hydrogen is necessary according to the equilibrium conditions and also to provide for the necessary heat of the endothermic reaction. At ambient pressure considerable reduction will take place at temperatures as low as about 900 K. However, at pressures of about 40 bar (which is the

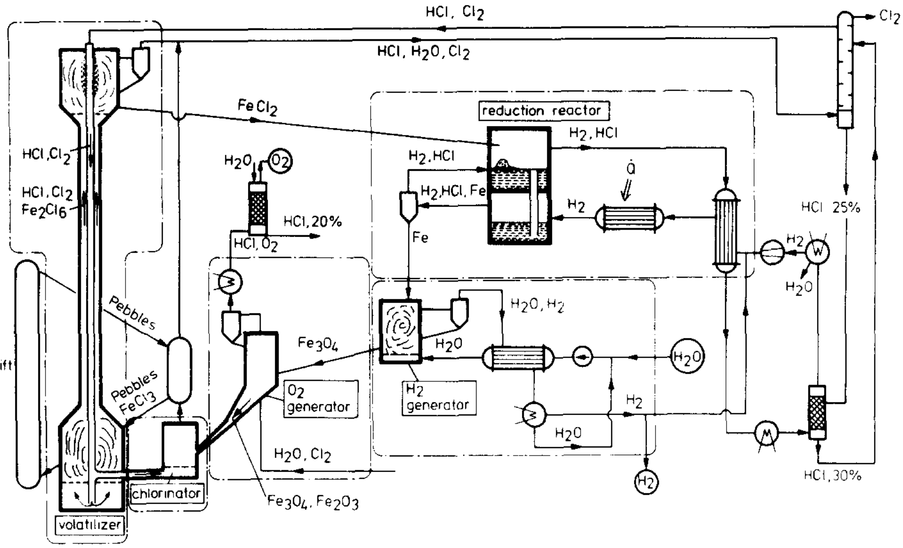

FIG. 1. Thermochemical water splitting process; iron–chlorine family.

pressure level of the coolant in a HTGR) sufficient yield of products can be achieved only at temperatures of about 1150 K. On the other hand, at 1150 K and 40 bars the energy required for reduction is not as much as for 900 K and 1 bar, because the reactant $FeCl_2$ exists in the liquid phase and therefore does not require the energy of melting, which of course is necessary when the reduction takes place at a temperature of 900 K where $FeCl_2$ exists in the solid phase. Tables 3 and 4 show the specific mass flows of the reactants and the products. At atmospheric pressure the reduction has to be conducted in two subsequent steps in order to achieve the mass flow of hydrogen indicated in Table 3. The iron is produced preferably from the vapour phase of $FeCl_2$ and must be separated from the gas flow.

Operating the cycle at 40 bar the hydrogen flow is increased compared with a cycle at ambient pressure, though the specific energy requirements are less. This is due to the lower yield of the products according to the equilibrium conditions at higher pressures.

The helium which leaves the heat exchanger at a temperature of about 900 K (resp. 1150 K at 40 bar), must be cooled further before entering the high temperature reactor. Because in this version of a closed cycle, process heat is required also at a relatively low temperature level in the form of low grade steam, it is desirable to incorporate a steam generator and a turbine in the overall process. This steam process has not been included in the flow diagram.

Hydrogen generation

The hydrolysis of iron with steam according to the chemical equation

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

is an exothermic reaction which—with respect to yield—is most favourable at low temperatures. At higher temperatures only part of the water vapour reacts with iron and the rest has to be separated by means of condensation. In a 2-step reaction the necessary amount of steam will be much smaller compared with the 1-step hydrolysis. The equilibrium conversion does not depend upon the pressure and therefore the mass flows at 40 bar and atmospheric pressure must not necessarily be different. The differences of mass flows as shown in Tables 3 and 4 are due to different ways of internal heat recovery.

Because the hydrolysis reaction takes place very close to chemical equilibrium, the loss of availability including those in the heat exchangers is comparatively small.

TABLE 3. Mass and energy balance of iron–chlorine cycle (1 bar)

REACTOR	DOMINANT REACTION	MATERIAL FLOW ENTERING			MATERIAL FLOW LEAVING			ENERGY EXCHANGE	
			moles/mole$_{H_2}$	Temp K		moles/mole$_{H_2}$	Temp K	kJ/mole$_{H_2}$	Temp Level K
REDUCTION	$FeCl_2 + H_2 \longrightarrow Fe + 2HCl$	H_2 $FeCl_2$	40 3	300 700	H_2 HCl Fe	37 6 3	380 380 900	531 (nuclear heat)	900 ÷ 1330
HYDROLYSIS	$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$	Fe H_2O	3 6.4	900 400	Fe_3O_4 H_2O H_2	1 2,4 4	1300 420 420	-	-
OXYGEN GENERATOR	$Cl_2 + H_2O + Fe_3O_4 \longrightarrow \frac{1}{2}O_2 + 2HCl + Fe_3O_4$	H_2O Cl_2 Fe_3O_4	5 1.2 1	380 400 1300	H_2O Cl_2 HCl O_2 Fe_3O_4	4 0,2 2 0,5 1	400 400 400 400 400	-	-
CHLORINATOR	$Fe_3O_4 + 8HCl + \frac{1}{2}Cl_2 \longrightarrow \frac{3}{2}Fe_2Cl_6 + 4H_2O$	Fe_3O_4 HCl Cl_2 Fe_2Cl_6	1 20 1.25 -	400 630 630 -	H_2O HCl Cl_2 Fe_2Cl_6	4 12 0,75 1,5	700 700 700 700	-	-
VOLATILIZER	$Fe_2Cl_6 \longrightarrow 2FeCl_2 + Cl_2$	Fe_2Cl_6 HCl Cl_2 H_2O	1.5 22 1.4 -	600 300 300 -	Fe_2Cl_6 HCl Cl_2 H_2O $FeCl_2$	- 20/2 1,2/1,6 - 3	- 630/400 630/400 - 700	61 (heat)	650
STEAM PROCESS		He H_2O, l	59 8	900 380	He H_2O, g	59 8	550 380	+432 (nuclear) -125 (electricity)	550 ÷ 900

TABLE 4. Mass and energy balance of iron–chlorine cycle (40 bar)

REACTOR	DOMINANT REACTION	MATERIAL FLOW ENTERING			MATERIAL FLOW LEAVING			ENERGY EXCHANGE	
			moles/mole$_{H_2}$	Temp K		moles/mole$_{H_2}$	Temp K	kJ/mole$_{H_2}$	Temp Level K
REDUCTION	$FeCl_2 + H_2 \longrightarrow Fe + 2HCl$	H_2 $FeCl_2$	62 3	350 950	H_2 HCl Fe	59 6 3	420 420 1150	+ 386 (nuclear heat)	1150 ÷ 1350
HYDROLYSIS	$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$	Fe H_2O	3 4	1150 300	Fe_3O_4 H_2	1 4	1300 350	+299 (heat) - 66 (heat)	523 1300 ÷ 1100
OXYGEN GENERATOR	$\frac{3}{2}H_2O + \frac{3}{2}Cl_2 + Fe_3O_4 \longrightarrow \frac{1}{2}O_2 + 3HCl + 1{,}5\,Fe_2O_3$	H_2O Cl_2 Fe_3O_4	4.8 1.9 1	430 430 1300	H_2O Cl_2 HCl O_2 Fe_2O_3	3,3 0.4 3 0.5 1.5	450 450 450 450 1100	-	-
CHLORINATOR	$Fe_2O_3 + 6HCl \longrightarrow Fe_2Cl_6 + 3H_2O$	Fe_2O_3 HCl Cl_2 Fe_2Cl_6	1.5 25.6 1.5 0.4	1100 580 580 580	H_2O HCl Cl_2 Fe_2Cl_6	4.5 16.6 1.5 1.9	700 700 700 700	-	-
VOLATILIZER	$Fe_2Cl_6 \longrightarrow 2FeCl_2 + Cl_2$	Fe_2Cl_6 HCl Cl_2 H_2O	1.9 16.6 1.5 4.5	700 700 700 700	Fe_2Cl_6 HCl Cl_2 H_2O $FeCl_2$	0.4 16.6 1.5 4.5 3	580 450 450 450 950	+ 375 (nuclear heat) + 66 (heat) -299 (heat) -76 (heat)	600 ÷ 1150 1100 ÷ 1300 523 580 ÷ 350

Oxygen generation and chlorination of iron oxide

The oxygen production according to the reverse Deacon process

$$Cl_2 + H_2O = 2HCl + \frac{1}{2}O_2$$

is an endothermic high temperature reaction. The heat requirement can be balanced by the internal energy of the hot iron (II, III)-oxide, produced in the hydrolysis reactor. Alternatively, if brought into direct contact with Fe_3O_4, the reaction products oxidize the iron (II, III)-oxide to iron (III)-oxide according to the equation

$$2Fe_3O_4 + \frac{1}{2}O_2 = 3Fe_2O_3,$$

and the heat of this exothermic reaction is sufficient to balance the necessary heat for the reverse Deacon process.

Within the cycle at 1 bar the energy requirement of the reverse Deacon process is balanced only by the internal energy of the hot iron (II, III)-oxide, whereas at 40 bar the iron (II, III)-oxide is oxidized to iron (III)-oxide for the same purpose. The reaction performance in both cases has to be adjusted in an appropiate manner which is not shown in the flow sheet (Fig. 1). Besides in the 40 bar cycle the necessary quenching of the product gas of the reverse Deacon process is done with part of the reactants streams for this process.

Both oxides, Fe_3O_4 and Fe_2O_3, can be chlorinated with hydrochloric acid according to

$$Fe_3O_4 + 8HCl + \frac{1}{2}Cl_2 = \frac{3}{2}Fe_2Cl_6 + 4H_2O$$

$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O$$

At 40 bar both oxides can be chlorinated with sufficient yield, whereas at atmospheric pressure the equilibrium yield of the second reaction is rather low for technical application.

Therefore, in the reverse Deacon process at atmospheric pressure, the iron (II, III)-oxide has to be conducted in such a way, that it does not come into contact with oxygen, whereas at higher pressures it is advantageous to oxidize Fe_3O_4 and use the heat of this exothermic reaction.

After chlorination, Fe_2Cl_6 is separated from the product gas by condensation. Therefore, the product gas has to be cooled either in a recuperative heat exchanger or by using a pebble heater.

Thermal decomposition of Fe_2Cl_6

Fe_2Cl_6 is vapourized and the vapour decomposes according to the equation

$$Fe_2Cl_6 = 2FeCl_2 + Cl_2$$

This reaction is exothermic. The equilibrium yield of chlorine is below 10%; therefore the Fe_2Cl_6 has to be recycled for complete decomposition, which is done by subsequent condensation and vaporization in the volatilizer the top of which is operated as a hot–cold apparatus. The Fe_2Cl_6 vapour condenses to $FeCl_3$ in the cold region which is cooled by the HCl and Cl_2 stream entering the volatilizer; subsequently the recycled $FeCl_3$ is vapourized again.

CONCLUSIONS

Complete recycling of all the products in the process needs the separation of mixtures containing chlorine, hydrochloric acid and water. This separation can be done by conventional techniques.

The transportation of the solid compounds can be achieved by gravity only, because the iron is transported in the upward direction only in the vapour phase Fe_2Cl_6.

Tables 3 and 4 also show the losses of availability in the main apparatus. Each balance has been calculated with reference to the balance sheets which are indicated in the flow sheet (Fig. 1) by dash-and-dot lines. The underlying data are taken from the thermochemical properties compilation of Barin & Knacke [4]. Additional losses have to be expected from the separation of chlorine, hydrochloric acid and water.

The overall efficiencies—the ratio of the higher heating value of the produced hydrogen and the enthalpy change of the helium stream—are 42.5% for the 1 bar cycle including electricity generation (cf. last line of Table 3) and 41.8% for the 40 bar cycle.

REFERENCES

1. H. CREMER, J. SCHUBERT, G. STEINBORN, T. RITTERBEX & K. F. KNOCHE, Water splitting processes of the iron–chlorine family, Proc. III/19, BNES Conf.: The high temperature reactor and process applications, London 26–28 Nov. 1974.
2. K. F. KNOCHE & J. SCHUBERT, Theoretische Untersuchung zur Erzeugung von Wasserstoff durch thermische Zersetzung von Wasser in Mehrstufenprozessen, Bericht zum Studienvertrag 045-72-7 ECID (f) der Europäischen Gemeinschaft, Aug. 1973.
3. J. SCHUBERT, Thermische Wasserzersetzung. Rechenverfahren zur Emittlung von Mehrstufenprozessen. Diss. RWTH Aachen, 1973.
4. I. BARIN & O. KNACKE, *Thermochemical Properties of Inorganic Substances* Berlin, Heidelberg, New York (1973).