Computer simulation of radiation damage in NaCl using a kinetic rate reaction model

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Abstract. Sodium chloride and other alkali halides are known to be very susceptible to radiation damage in the halogen sublattice when exposed to ionizing radiation. These radiolysis mechanisms have been studied for many years and the primary process, the production of F and H centres, is well understood now. The secondary processes of defect clustering are less well understood but there is substantial experimental evidence that, at temperatures above room temperature, F centres can coagulate and form metallic alkali colloids and that H centres will cluster, giving rise to the formation and growth of dislocation loops.

The formation of radiation damage in NaCl has generated interest because of the relevance of this damage to the disposal of radioactive waste in rock salt formations. In order to estimate the long-term behaviour of a rock salt repository, an accurate theory describing the major processes of radiation damage in NaCl is required. In 1977, Jain and Lidiard presented a rather simple model which, until now, has served as a means for long-term predictions of rock salt repositories. Although the model of Jain and Lidiard describes many experimental results on colloid growth in NaCl reasonably well, it describes the early stages of colloid growth and the effect of impurities on colloid growth less well. The model presented in this paper is an extended version of the Jain–Lidiard model; its extensions comprise the effect of impurities and the colloid nucleation stage on the formation of radiation damage. The new model has been tested against various experimental data obtained from the literature and accounts for several well known aspects of radiation damage in alkali halides which were not covered by the original Jain–Lidiard model. The new model thus may be expected to provide more reliable predictions for the build-up of radiation damage in a rock salt nuclear waste repository.

1. Introduction

In several countries, which include the Netherlands, Germany and the USA, rock salt formations are considered as possible repositories for the permanent disposal of high-level radioactive waste. There are many problems which have to be solved before a nuclear waste repository in a rock salt formation can be taken into operation. One of these problems is the effect of radiation on the salt. It is generally known that gamma irradiation in alkali halides such as NaCl, can produce defects in the form of F and H centres. Furthermore, it is known that the F centres may cluster and build small aggregates in the form of M (= F_2), R (= F_3) and N (= F_4) centres and large aggregates in the form of sodium colloids. Besides, the H centres may aggregate in the form of molecular Cl_2 centres. One of the risks that has to be investigated very thoroughly in respect of the disposal of nuclear waste is the possibility of a sudden back reaction of the Na colloids and the molecular Cl_2 that can be produced in a rock salt formation under irradiation. Such a back reaction, which would take place if the concentration of Na colloids and molecular Cl_2 exceeds a certain percolation threshold, might entail an explosive release of the stored chemical energy and

cause a serious deterioration of the near field integrity of the repository. This risk assessment requires a model describing the long term (i.e. over 10^6 years) effects of radiation at rather low dose rates (less than 10^{-1} Mrad hr^{-1}) on rock salt.

The study of defects in alkali halides has a history that started about a century ago and many aspects of radiation induced defect formation are well understood now. Among the numerous types of defect centres that one can come across in alkali halides, the F centre has received most attention [1]. The first indications for the precipitation of F centres into colloids were observed by McLennan [2] and Westerveld [3] and since that time, a steady progress in this field has been reported [1,4–6].

In 1977, Jain and Lidiard presented the first theoretical modelling of colloid formation in NaCl [7]. This model, based on kinetic rate reactions, was extended in 1979 [8]. It indicated that in the process of accumulation of radiation damage, the temperature and the dose rate play a major role. Van Opbroek and Den Hartog [9] have elucidated these aspects of the model. In 1985, Bergsma *et al* presented the first Jain–Lidiard model calculations of radiation dose deposition and colloid formation in a rock salt nuclear waste repository [10]. These calculations indicated that, in the proposed set up for a nuclear waste depository, the maximum colloid fraction in the rock salt would not exceed 7 mol%. This number is rather reassuring, but doubt can be cast on the reliability of the Jain–Lidiard model in describing the radiation induced damage formation in rock salt. For example, the model does not take into account the effects of: (i) impurities, (ii) the nucleation stage of colloids, (iii) strain and (iv) grain boundaries.

It is a well established fact that the presence of impurities can significantly enhance the production of F centres in alkali halides under irradiation [11]. The generally accepted mechanism underlying this effect is that the impurities act as traps for the H centres and thus prevent their recombination with the F centres [12]. Agulló-López and Jaque have suggested a model for this mechanism [13] which has proved to be successful in describing the experimentally observed colouring curves in alkali halides [14–17]. It can be expected that the presence of impurities thus leads to higher model predictions of the maximum colloid fraction that can be achieved in the rock salt.

The presence of dimers and trimers of F centres in irradiated alkali halides has also been investigated very intensively in the past [18] and, e.g., it is a well established fact that at room temperature, the concentration of M centres is proportional to the square of the F centre concentration [19,20]. Hodgson [21–23] successfully modelled this relation by a kinetic rate reaction in order to explain the F- and M-centre colour curves in NaCl during irradiation at temperatures between 15 and 95 °C. For the R and N centres, similar rate equations can be established although there exist less experimental data on the growth of these defects [6].

The effect of plastic deformation on the defect growth under irradiation has been investigated less thoroughly than the topics mentioned before. Experiments of Levy, Swyler *et al* with synthetic NaCl crystals, strained before irradiation show that this strain significantly enhances the growth of colloids [24]. Durand *et al* observed the same effect in additively coloured KCl [25]. In their calculations, Jain and Lidiard [7] have taken a fixed number for the concentration of dislocation loops (C_l) derived for unstrained crystals, but evidently, in simulations of rock salt formations, C_l must be a function of the local strain.

The effect of grain boundaries on the defect formation has two aspects. One is the enhanced diffusion of defects along the grain boundary [26] a process which might enhance the formation of colloids; the other is due to the presence of intergranular brine in salt [27], a substance which will surely inhibit the growth of clusters of defects [28]. At this moment,

however, there is insufficient experimental information on brine enhanced recrystallization to realize a proper theoretical implementation of this effect.

Recently, Groote and Weerkamp [6] presented a revised version of the Jain–Lidiard model in which some aspects of the role of impurities and colloid nucleation on the build-up of radiation damage in NaCl were implemented. In this model, which was recently presented in a slightly revised form by Seinen *et al* [29], the role of impurities was modelled following the H-centre trapping mechanism suggested by Agulló-Lopez and Jaque [13]. In the model of Groote and Weerkamp the nucleation stage of colloids is represented by the formation of dimers and trimers of F centres via a process of self-trapping.

The new model presented in this paper incorporates both the main elements of the original Jain–Lidiard model and the mentioned extensions of Groote and Weerkamp. The last authors also introduced a mechanism called 'dislocation line thickening' which should account for an enhanced flux of F and H centres to the dislocation lines after the moment that the dislocation line density has reached its maximum. Although the validity of the original Jain–Lidiard theory certainly is limited for crystals with a large fraction of radiation damage, there is very little theoretical and experimental evidence for this 'thickening' mechanism and therefore it has not been implemented in the new model. Instead, a back reaction of F centres with molecular chlorine centres, as suggested by Lidiard [8], has been implemented. With this back reaction, saturation of colloid fractions at very high doses and annealing experiments at elevated temperatures are well described. Furthermore, the new model has been validated for a number of experimental data on radiation damage in NaCl found in the literature.

2. Model

2.1. Physical basis

The model starts with the radiation-induced formation of Frenkel pairs consisting of stable F and H centres. The physical processes that precede this birth of defect pairs, i.e. the formation and radiationless decay of self-trapped excitons [30, 31] will be ignored. The defect pair production is assumed to be a linear function of the dose rate. In their model, Jain and Lidiard [7] also assumed that the defect pair production is independent of the temperature. In general, the net yield of stable F–H pairs is equal to $P_s \eta_F$, where η_F is the quantum yield of primary F–H pairs and P_s is the fraction of these defects that will survive direct recombination and become a distant F–H pair [31]. For low temperatures, P_s is a function of the temperature, but Kotomin *et al* [32] have shown that for the temperatures to be considered in this work ($T > 0\,°C$), this fraction becomes constant. For the temperature range 130–220 K, Sonder [33, 34] has shown that for NaCl and other alkali halides the production of primary Frenkel pairs can be described by an Arrhenius law:

$$\eta_F = \eta_F^0 \exp(-E_c/kT). \tag{1}$$

The activation energy E_c is 0.07 eV for NaCl. Unfortunately, no experimental data on η_F for temperatures above 250 K are available and since Sonder's data suggest a levelling off for η_F for NaCl above 225 K, we will follow the assumption of Jain and Lidiard and consider $P_s \eta_F$ as temperature independent in this work. Sonder's data, however, also suggest that the total energy needed to create an uncorrelated F–H pair near room temperature is about 100 eV. Jain and Lidiard used a value of 15 eV, which is more appropriate for KCl. In this work, Sonder's value will be used, which implies that a dose rate of 1 Mrad hr^{-1} corresponds with 1.667×10^{-8} dpa s^{-1}.

After the creation of a defect pair, the following reactions can be discerned.

2.1.1. Recombination of F and H centres. This process is dominated by the diffusion coefficient of the H centres which will be discussed below.

2.1.2. Diffusion of F centres. The general expression for the thermally activated mobility is:

$$D_F = D_F^0 \exp(-E_F/kT) \qquad cm^2 \ s^{-1}. \tag{2}$$

Despite the many studies of F centres, the mobility D_F in NaCl is still not known very accurately. Comparison with experimental data on the saturation density of F centres led Jain and Lidiard to the assumption that the most probable value for the activation energy for the diffusion of F centres, E_F is 0.80 eV. From experimental data on M-centre production by means of F-centre thermal diffusion, Hodgson *et al* [23] concluded that the activation energy is 0.88 ± 0.13 eV. Hughes and Lidiard [35] compared the saturation values of the F-centre concentrations as reported by various authors with the predictions of the original Jain–Lidiard model. The authors found that the value of 0.80 eV gave rise to model predictions of c_F^{sat} that were too high and they show that a value of 0.66 eV for E_F yields better model predictions. In the original Jain–Lidiard model however, the formation of M, R and N centres was not taken into account. In the next section it will be shown that these reactions reduce the concentration of free F centres such that with a value of 0.80 eV for E_F, the model predictions of c_F^{sat} are in good agreement with experimental results. Jain and Lidiard have used a value of 10^{-2} cm^2 s^{-1} for the pre-exponential factor of the diffusion coefficient D_F^0. In this work, D_F^0 has been adjusted in order to obtain an optimum correspondence between the model and experimental data. The results of this adjustment will be discussed in the next section.

2.1.3. Trapping of F centres and colloid growth. F centres can be trapped by dislocation lines. It is estimated [7] that this trapping has an efficiency that is about 10% less than the efficiency of H-centre trapping by dislocation lines. The nucleation stage of colloids in NaCl is still not understood very well and therefore has to be modelled in a rather rudimentary way. It is assumed that the nucleation of colloids can take place both heterogeneously and homogeneously. The homogeneous nucleation occurs by self-trapping of F centres, a process which leads to aggregation into M (= F_2), R (= F_3) and N centres. Although there is no conclusive proof for the structure of N centres yet [36], in this work it will be assumed that N centres consist of four F centres. Moreover, in the model, N centres act as colloid nuclei. From irradiation experiments, we know that the concentration of R and N centres is always at least several orders of magnitude smaller than the M-centre concentration. Calculations of Jain [37] have shown that the binding energy of an R centre with respect to an M and F centre is very small (about 0.1 eV for NaCl). In this paper we will assume that the formation of both R and N centres is energetically less favourable than the M-centre formation. With respect to the formation rate of M centres, the formation rate of R and N centres, K_R, is therefore reduced by a temperature-dependent factor suggested by Groote and Weerkamp.

The heterogeneous nucleation is the precipitation of F centres at sites other than N centres. The nature of these sites will remain unspecified in this paper, but it can be assumed that the concentration of these nuclei is related to the concentration of impurities and dislocation lines [4]. After nucleation, the colloids are assumed to be particles with a Euclidean dimension and a mean radius $r_c(t)$. Investigation by electron microscopy suggests that the colloidal precipitates retain the FCC structure of the original Cl sublattice rather than the normal BCC structure of the Na metal [38]. The growth process of the colloids

is basically an aggregation of F centres via random walk, so one might expect that this process could be described in terms of the diffusion limited aggregation (DLA) theory [39]. According to this theory, the colloids would have a non-Euclidean, fractal dimension of approximately 2.52. It has been shown that the outcome of the Jain–Lidiard model depends strongly on the dimension of the colloids [40] but so far there is no experimental evidence for a non-Euclidean dimension of colloids in NaCl, either from electron microscopy [38] or from neutron diffraction experiments [41]. In addition it should be mentioned that recently DLA simulations have been presented in which the centre of the 'launching boundary' was not fixed at the nucleation site but was set randomly at a site of the growing cluster [42]. These simulations, which seem to be more appropriate for the aggregation of F centres in NaCl than the original DLA model, give rise to clusters with an Euclidean dimension.

2.1.4. Emission of F centres from M centres and colloids. The emission of F centres from colloids is a thermally activated process, governed by an activation energy of 0.3 eV [43]. If $c_F^{(e)}$ is the concentration of F centres in equilibrium with colloids, precipitation of F centres into colloids will take place as long as the F-centre concentration (c_F) is larger than $c_F^{(e)}$. This implies that, for a given dose rate, there is a temperature T_e for which $c_F^{(e)}(T_e) = c_F(T_e)$ and that for temperatures larger than T_e, no colloid formation can take place. The linear relation between the M-centre concentration and the square of the F-centre concentration, experimentally observed [22, 23, 34] at temperatures below 50 °C, is related to the dissociation of M centres. In the next section it will be reasoned that this relation implies that the dissociation rate of M centres, $K_M^{(e)}$, is proportional to the formation rate of M centres, K_F. Using experimental data on c_F and c_M by Hodgson, the ratio between $K_M^{(e)}$ and K_F is determined to be approximately equal to 2×10^{-3}. The dissociation of R and N centres, finally, is incorporated in the net production rate K_R.

2.1.5. Diffusion of H centres. The thermally activated mobility of the H centres (D_H) in NaCl is also not known very accurately yet. For the modelling of the colloid growth, this is not very important though, since it will be shown in the next section that the growth rate is insensitive to D_H. It is a well-established fact that D_H is much larger than D_F (by about ten orders of magnitude). In practice this means that we may assume that the concentration of H centres is always in equilibrium. Adopting the values for the pre-exponential factor and the activation energy from Jain and Lidiard, we will use the following relation for the diffusion coefficient:

$$D_H = 10^{-2} \exp(-0.1 \, \text{eV} \, kT) \qquad \text{cm}^2 \, \text{s}^{-1}. \tag{3}$$

2.1.6. Trapping of H centres and growth of dislocation loops. After their creation, the H centres not only recombine with F centres and colloids; they can also be trapped by impurities or may aggregate to clusters of H centres. The rate equations as suggested by Agulló-López and Jaque [13] will be used for the modelling of the trapping of H centres by impurity traps. This H-centre trapping leads to the formation of S_1, S_2 and S_3 complexes, which are combinations of an impurity with respectively one, two and three H centres. An S_3 centre is considered to be thermally stable and acts as the beginning of a new dislocation loop. The S_1 and S_2 centres thermally emit H centres. There is very little theoretical or experimental information on the equilibrium concentrations $c_{H,S_1}^{(e)}$ and $c_{H,S_2}^{(e)}$, so we have adopted the values suggested by Groote and Weerkamp. Dislocation lines act as sinks for both F and H centres, but the drain of the vacancy defects will be smaller than that of the interstitial defects. Experience with irradiated metals has led Jain and Lidiard to the

assumption that this bias coefficient $(z_H - z_F)/z_F$ is approximately 10%. According to Hobbs *et al* [38], pairs of H centres in the near vicinity of dislocation lines will form molecular Cl_2 centres by 'digging out' NaCl molecules from their regular position. These NaCl molecules now move to the extra plane, giving rise to dislocation loop growth. According to Catlow *et al* [44] the mechanism is an exothermic reaction by 3–3.5 eV.

2.1.7. Recombination of F centres with molecular Cl_2 centres. The original model of Jain and Lidiard contained no mechanism for a saturation of the colloid growth since the dislocation sinks are assumed to be unsaturable. The experiments of Jenks and Bopp [45], however, markedly suggest a saturation of the colloid growth at relatively high integrated doses (50 Grad for $K = 10$ Mrad hr^{-1}). In order to account for this saturation, Lidiard [8] proposed an *ad hoc* back reaction of F centres with molecular Cl_2 centres. The rate of the reaction is Arrhenius like:

$$\gamma = \gamma_0 \exp(-E_\gamma/kT). \tag{4}$$

This reaction is adopted in the present model but instead of using the values for γ_0 and E_γ as suggested by Lidiard, these parameters have been adjusted such that a maximum correspondence between model predictions and experimental results found in the literature, was obtained. This validation of the model will be discussed in the next section.

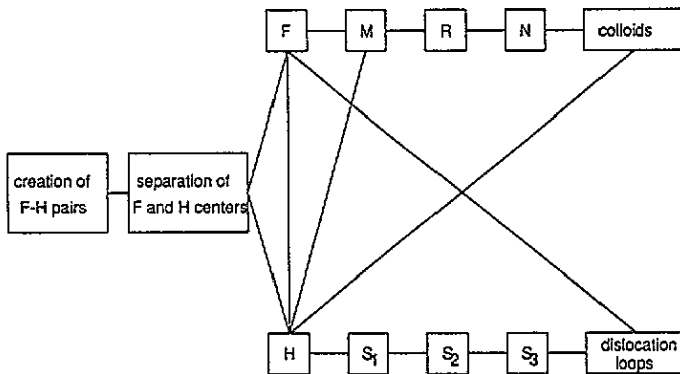A survey of the different reaction mechanisms which have been incorporated in the model, is given in figure 1.

Figure 1. Scheme of the reactions.

2.2. Rate equations

The mechanisms discussed in the preceding section lead to the following rate equations:

$$dc_F/dt = K + 2K_M^{(e)}c_M - 2K_Fc_Fc_F - K_Fc_Fc_M - K_Fc_Fc_R - K_Fc_Fc_N + K_Hc_Hc_M$$
$$- 4\pi r_c C_c D_F(c_F - c_F^{(e)}) - K_2c_Fc_H - z_F\rho_d D_Fc_F - \gamma D_Fc_Fc_{Cl_2}. \tag{5}$$

The first term on the right-hand side describes the production rate of F and H centres due to irradiation. See also tables 1 and 2. The next five terms describe the disintegration of an M centre and the trapping of F centres by F, M, R and N centres respectively. The seventh term accounts for the annihilation reaction of an H centre at an M centre. It is assumed that the loss of F centres to colloids and the evaporation of F centres from colloids are controlled by bulk diffusion processes. This leads to the term $4\pi r_c D_F C_c(c_F - c_F^{(e)})$. $K_2c_Fc_H$

Table 1. List of symbols.

Parameter	Definition
c_F	fraction of F centres
c_M	fraction of M centres
c_R	fraction of R centres
c_N	fraction of N centres
c_A	fraction of Na in colloids
c_H	fraction of H centres
c_{S_0}	fraction of impurities
c_{S_1}	fraction of single H centres trapped at impurities
c_{S_2}	fraction of H dimers trapped at impurities
c_{S_3}	fraction of H trimers trapped at impurities
c_{Cl_2}	fraction H centres converted into molecular Cl_2 centres
$c_F^{(e)}$	fraction F centres in equilibrium with colloids
$c_{H,S_1}^{(e)}$	fraction H centres in equilibrium with S_1 centres
$c_{H,S_2}^{(e)}$	fraction H centres in equilibrium with S_2 centres
K	production rate of uncorrelated F–H pairs
K_F	rate constant for the formation of M centres and colloids
K_R	rate constant for the formation of R and N centres
K_2	rate constant for the recombination of F and H centres
K_H	rate constant for the formation of S_n clusters
$K_M^{(e)}$	dissociation rate of M centres
D_F	diffusion coefficient of F centres
D_H	diffusion coefficient of H centres
r_c	mean radius of Na colloids
C_c	number of colloids per cm^3
z_F	dislocation bias coefficient for F centres
z_H	dislocation bias coefficient for H centres
ρ_d	dislocation line density
γ	rate coefficient for back reaction between F centres and molecular Cl_2
N	number of Na^+ ions in NaCl per cm^3
C_l	number of dislocation loops per cm^3
C_l^0	number of nuclei for dislocation loops per cm^3 at $t = 0$
ρ_0	dislocation line density at $t = 0$
b	Burgers' vector of dislocation loops in NaCl
ν	ratio of molecular volume of NaCl and atomic volume of metallic Na

is the back reaction between F centres and H centres; $z_F \rho_d D_F c_F$ is the loss of F centres to dislocation loops, and the last term describes the back reaction between F centres and Cl_2 molecules.

Having described all the terms in the kinetic rate reaction of the F-centre concentration, the other rate reactions are more or less self-explanatory and are given with only a few comments.

$$dc_M/dt = K_F c_F c_F - K_H c_H c_M - K_M^{(e)} c_M - K_R c_F c_M. \tag{6}$$

At low temperatures (i.e. below room temperature) M-centre growth is very slow. Since the growth rate of R centres ($K_R c_F c_M$) is even smaller, we may assume that in this temperature regime: $K_F c_F c_F - K_H c_H c_M - K_M^{(e)} c_M = 0$ or:

$$c_M = (K_F/(K_M^{(e)} + K_H c_H))c_F^2. \tag{7}$$

This is the linear relation mentioned in the preceding section. For higher temperatures, the formation of R centres cannot be neglected any more and the ratio between c_M and c_F^2

Table 2. Parameter values used in this work.

Parameter	Value	Reference
$K(\text{dpa s}^{-1})$	$1.667 \times 10^{-8} K$ (K in Mrad hr^{-1})	[11]
D_H (cm^2 s^{-1})	$1.0 \times 10^{-2} \exp(-0.10/kT)$	[7]
D_F (cm^2 s^{-1})	$1.5 \times 10^{-2} \exp(-0.80/kT)$	fit
K_F (s^{-1})	$10^{16} D_F$	[7]
K_2 (s^{-1})	$10^{14} \exp(-0.10/kT)$	[7]
K_R (s^{-1})	$K_F \exp(-0.20/kT)$	[6]
K_H (s^{-1})	$10^{16} D_H$	[7]
$K_M^{(e)}$	$2 \times 10^{-3} K_F$	[23]
$c_F^{(e)}$	$2 \times 10^{-4} \exp(-0.30/kT)$	[43]
$c_{H,S_1}^{(e)}$	$5 \times 10^{-10} \exp(-0.25/kT)$	[6]
$c_{H,S_2}^{(e)}$	$5 \times 10^{-10} \exp(-0.10/kT)$	[6]
C_c^0(cm^{-3})	10^{15}	[7]
z_F	1	[7]
z_H	1.1	[7]
ρ_0(cm^{-2})	10^5	[7]
γ (cm^{-2})	$1 \times 10^{18} \exp(-0.55/kT)$	fit
N (cm^{-3})	2.22×10^{22}	
C_I^0 (cm^{-3})	10^{15}	[7]
b (cm)	3.98×10^{-8}	
v	1.13	

ceases to be constant [23].

$$dc_R/dt = K_R c_F c_M - K_R c_F c_R \tag{8}$$

$$dc_N/dt = K_R c_F c_R - K_F c_F c_N \tag{9}$$

$$dc_A/dt = K_F c_F c_N + 4\pi r_c C_c (D_F c_F - D_H c_H - D_F c_F^{(e)}) \tag{10}$$

$$dc_H/dt = K - K_H c_{S_0} c_H - K_H c_{S_1} c_H - K_H c_{S_2} c_H + K_H c_{S_1} c_{H,S_1}^{(e)} + K_H c_{S_2} c_{H,S_2}^{(e)}$$
$$- z_H \rho_d D_H c_H - K_2 c_F c_H - 4\pi r_c C_c D_H c_H - K_H c_H c_M \tag{11}$$

$$dc_{S_1}/dt = K_H c_{S_0} c_H - K_H c_{S_1} c_{H,S_1}^{(e)} - K_H c_{S_1} c_H + K_H c_{S_2} c_{H,S_2}^{(e)} \tag{12}$$

$$dc_{S_2}/dt = K_H c_{S_1} c_H - K_H c_{S_2} c_{H,S_2}^{(e)} - K_H c_{S_2} c_H \tag{13}$$

$$dc_{S_3}/dt = K_H c_{S_2} c_H \tag{14}$$

$$dc_{Cl_2}/dt = \rho_d (z_H D_H c_H - z_F D_F c_F) - \gamma D_F c_F c_{Cl_2}. \tag{15}$$

The rate reaction for the concentration of empty traps of H centres is:

$$dc_{S_0}/dt = K_H c_{S_1} c_{H,S_1}^{(e)} - K_H c_{S_0} c_H \tag{16}$$

where at $t = 0$ the concentration of impurities is $c_{S_0}^0$. The number of colloids increases during irradiation because each N centre that traps an F centre is considered to be a new nucleus for a colloid. This gives rise to the following rate reaction:

$$dC_c/dt = N K_F c_F c_N. \tag{17}$$

At $t = 0$, there already is a number of unspecified colloid nuclei present in the salt; its number concentration is C_c^0.

According to the mechanism of Hobbs *et al*, a c_{S_3} centre is considered to be the beginning of a new dislocation loop. The number of dislocation loops therefore is:

$$C_l = C_l^0 + N c_{S_3}. \tag{18}$$

Jain and Lidiard have derived the following cross relations between the density of dislocation lines ρ_d and the concentration of molecular Cl_2 centres and between the mean colloid radius r_c and the colloid fraction c_A respectively:

$$\rho_d = \sqrt{((2\pi C_l/b)c_{Cl_2} + \rho_0^2)} \tag{19}$$

$$r_c = \sqrt[3]{(3c_A/4\pi\nu C_c)}. \tag{20}$$

Note that equations (19) and (20) have been derived for fixed values for C_l and C_c respectively and that their usage for varying values of C_l and C_c, as in this paper, is only approximately valid. Furthermore, the dislocation loops cannot grow infinitely but will join up into a network. If r_l is the mean loop length, a rough estimate for this to happen is [8]:

$$(4\pi/3)r_l^3 = 1/C_l. \tag{21}$$

With $\rho = 2\pi r_l C_l$, we obtain an approximation for the maximum dislocation line density:

$$\rho_m \simeq C_l^{2/3}. \tag{22}$$

3. Validation of the model

In the introduction it was mentioned that the main goal of the modelling effort is to enable a prediction of the growth of sodium colloids and molecular chlorine centres in a rock salt nuclear waste repository. Therefore, the model should in the first place give a reliable description of the available results of experiments concerning the formation of colloids and molecular Cl_2. Unfortunately, the larger part of the research on irradiated NaCl has been focused on F centres. Until now, only a few systematic studies on colloid formation have been reported, and the formation of molecular Cl_2 has only been studied indirectly; i.e. through the study of dislocation loop growth [46].

The experimental data that have been used for the validation of the present model were taken from the work of Jenks and Bopp [45] and Groote and Weerkamp [6]. Both sets of data deal with the formation of colloids in NaCl single crystals. Jenks and Bopp used a ^{60}Co source and performed irradiations at a constant dose rate of 10 and 40 Mrad hr^{-1}. After irradiation, they made calorimetric measurements with a Roux-type calorimeter in order to determine the stored energy build-up in the form of colloids and molecular Cl_2. Groote and Weerkamp used the electron beam from a Van de Graaff accelerator as a source for irradiations with a mean dose rate of 12 Mrad hr^{-1}. The stored energy was measured by differential scanning calorimetry experiments.

In the comparison of the experimentally observed stored energy and the theoretical mole fraction of colloids, a conversion factor of 125 J g^{-1} per mole% colloidal Na has been used. This value was obtained by Groote and Weerkamp as a result of comparing the stored energy, released in annealing experiments with the latent heat associated with the melting of the metallic Na in the same samples. The adjustment of the model was performed as
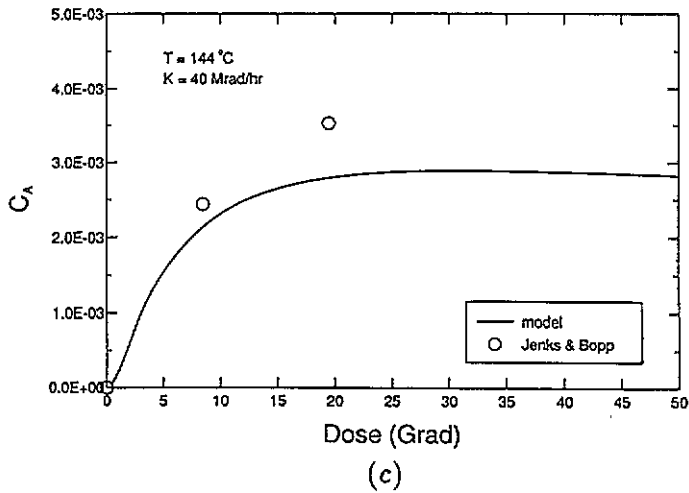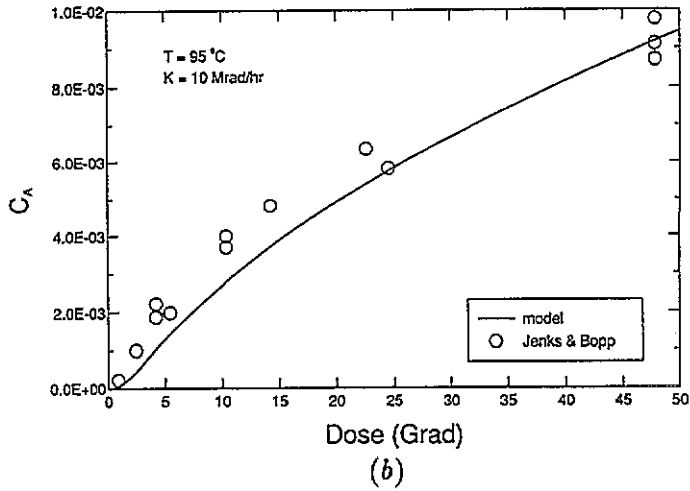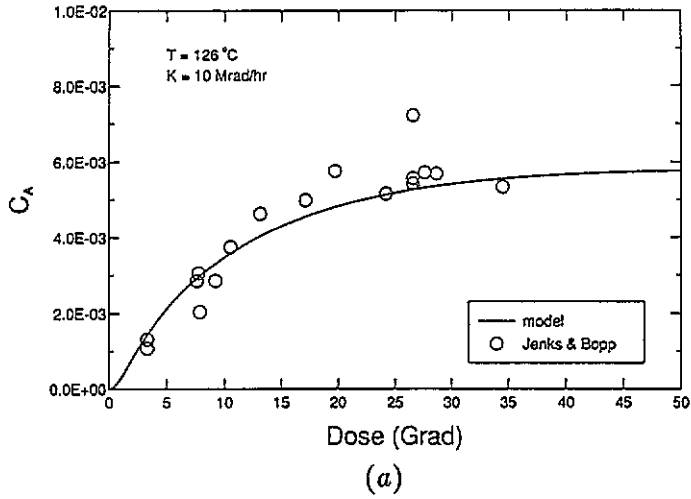
Figure 2. Comparison of the model with experimental data of Jenks and Bopp [45] on colloid formation.

follows. By a process of trial and error, the parameters D_F^0, γ_0 and E_γ were tuned, so that an optimum fit of the experimental data was obtained.

The results of this procedure are shown in figures 2 and 3. Note that for temperatures higher than 125 °C, Groote and Weerkamps' data suggest a very sudden decrease of c_A, where Jenks and Bopp measure significant amounts of stored energy at 126 °C and at 144 °C. Since the data of Jenks and Bopp are rather consistent for a number of integrated doses, whereas the data of Groote and Weerkamp refer only to one integrated dose value, the data of the first authors were given a larger weight in the tuning procedure. The tuning procedure has led to: $D_F^0 = 1.5 \times 10^{-2}$ cm^2 s^{-1}, $\gamma_0 = 1 \times 10^{-18}$ cm^{-2} and $E_\gamma = 0.55$ eV. (Note that Lidiard [8] has suggested the values of respectively 1.5×10^{-2} cm^2 s^{-1}, 3×10^{-18} cm^{-2} and 0.60 eV.) For a survey of other parameters used in the model, which were obtained from the literature, see table 2.
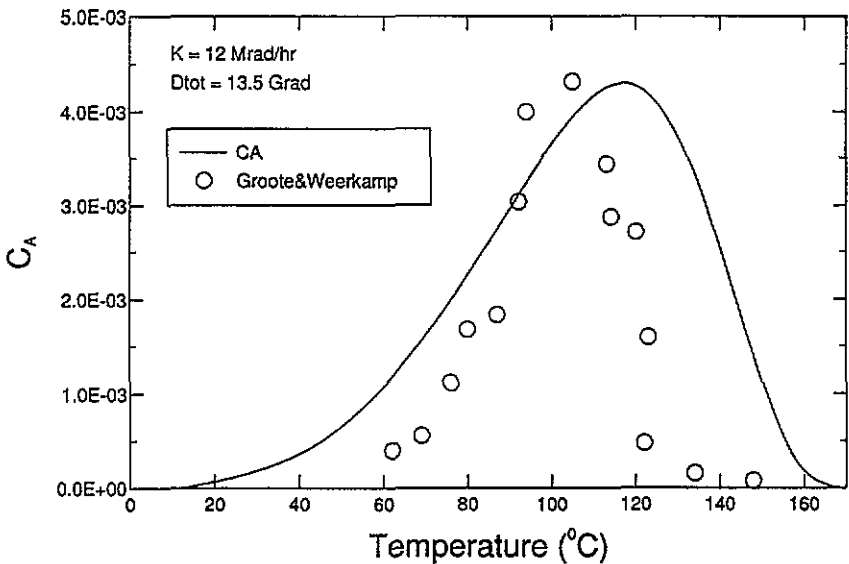

Figure 3. Comparison of the model with experimental data of Groote and Weerkamp [6] on F-colloid formation.

It can be observed that the model now describes the results of Jenks and Bopp reasonably well. Since there is a discrepancy between the data of Groote and Weerkamp and the data of Jenks and Bopp for temperatures above 100 °C, it is no surprise that the model does not fit the high-temperature data of the first authors well.

Comparison of experimental data on F-centre concentrations with model predictions would provide additional information on the validity of the values used for E_F and D_F^0. A complication for this comparison is that all the experimental data on the presence of F centre are obtained by optical absorption. The relation between the absorption coefficient and the defect concentration is given by Smakula's equation [18].

Usage of this equation however, requires among other things, knowledge of the oscillator strength f and the integral area of the F-centre absorption band. The oscillator strength depends on the local environment of the F centre so only an approximate value can be used for covering a range of concentrations of F centres and other defects. Furthermore, many experimentalists do not report the area or the FWHM of the absorption bands. Thus we are

forced to use a rough estimate of the relation between the optical absorption coefficient as found in the literature and the F-centre concentration. In figure 4, F-centre concentrations measured by Hodgson *et al* [21] are compared with the model using a conversion factor of 1 cm^{-1} optical density (OD) $\equiv 1 \times 10^{-4}$ mole% F centres. The data of Hodgson refer to synthetic NaCl, irradiated with 1.8 MeV electrons at 25 °C and 85 °C. It can be observed that there is good agreement between the experiments and the theory at lower temperatures but that at higher temperatures the saturation as predicted by the model, occurs too slowly. Comparison with data by Levy *et al* [24], does not give any indication that the theoretical saturation value of the F centres is too small. In figure 5, we have plotted model calculations and data by Levy which have been obtained for both synthetic NaCl and natural salt from Los Medanos (New Mexico, USA). Hughes and Lidiard [35] have compared these data of Levy with the original Jain–Lidiard model and came to the conclusion that the value of E_F needed an adjustment. From figure 5 it can be learned that the new model, with the original value for E_F, adequately describes the variation of the saturated F-centre concentration with the temperature.
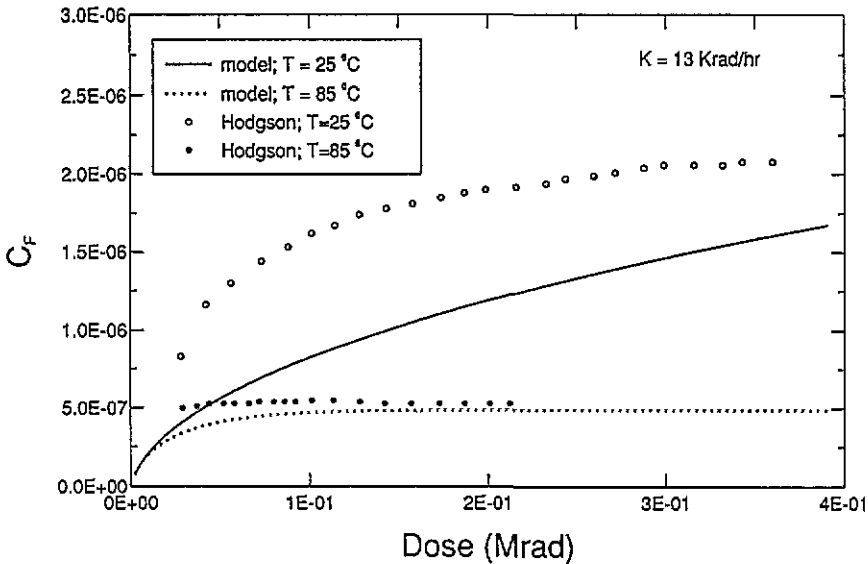

Figure 4. Comparison of the model with experimental data of Hodgson *et al* [21] on F-centre growth.

Finally, the relation between c_F^2 and c_M at low temperatures is evaluated. As mentioned above, there exists an experimentally confirmed linear relation between these two observables. In figure 6, model predictions of c_F^2 versus c_M at $T = 24$ °C are plotted. We see that the model predicts the correct linear relationship, even for the higher dose region were C_F decreases and the curve turns back in the direction of the origin.

4. Model predictions

4.1. Aggregation of F centres

If we look at the concentration of the F centres as a function of the dose, three regimes can be distinguished. In figure 7(*a*) this is illustrated for a dose rate of 1 Mrad hr^{-1} and two
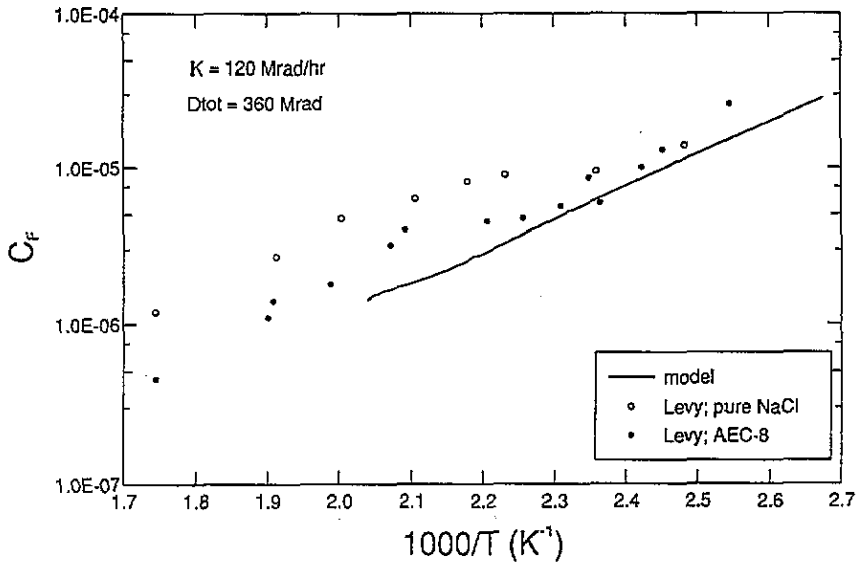
Figure 5. Comparison of the model with experimental data of Levy *et al* [24] on F-centre saturation.
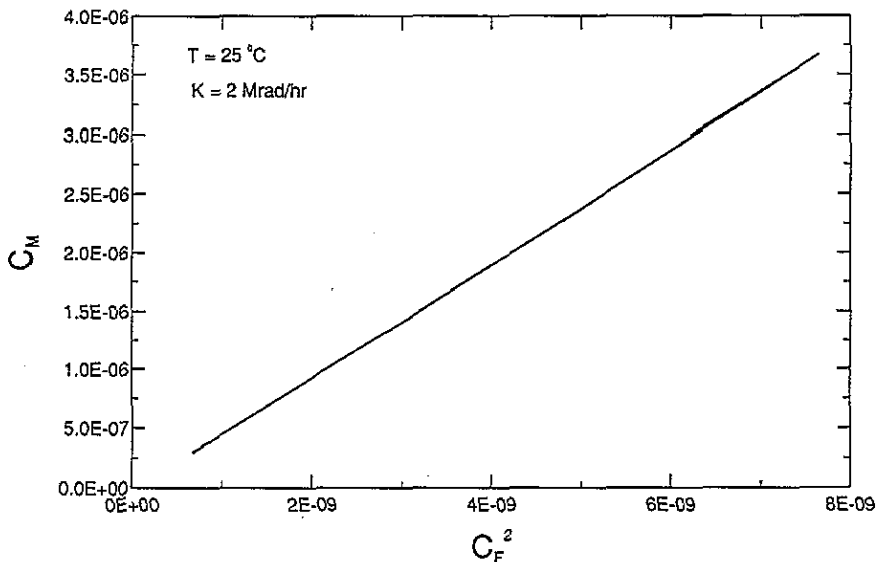

Figure 6. Fraction of M centres versus the square of the F-centre concentration.

different temperatures. Initially, c_F increases proportional to the dose D but very soon the increase is proportional to $\sqrt{D}$ (regime I) [7]. At higher doses, a new regime is entered and c_F reaches a saturation plateau (regime II). The level of this plateau is lower for higher temperatures. Neglecting the formation of M, R and N centres, it can be shown that the saturation level of the F centres is proportional to $\sqrt{(K/D_F)}$. If the irradiation continues, the third regime is entered. The aggregation of F centres now overwhelms the creation of
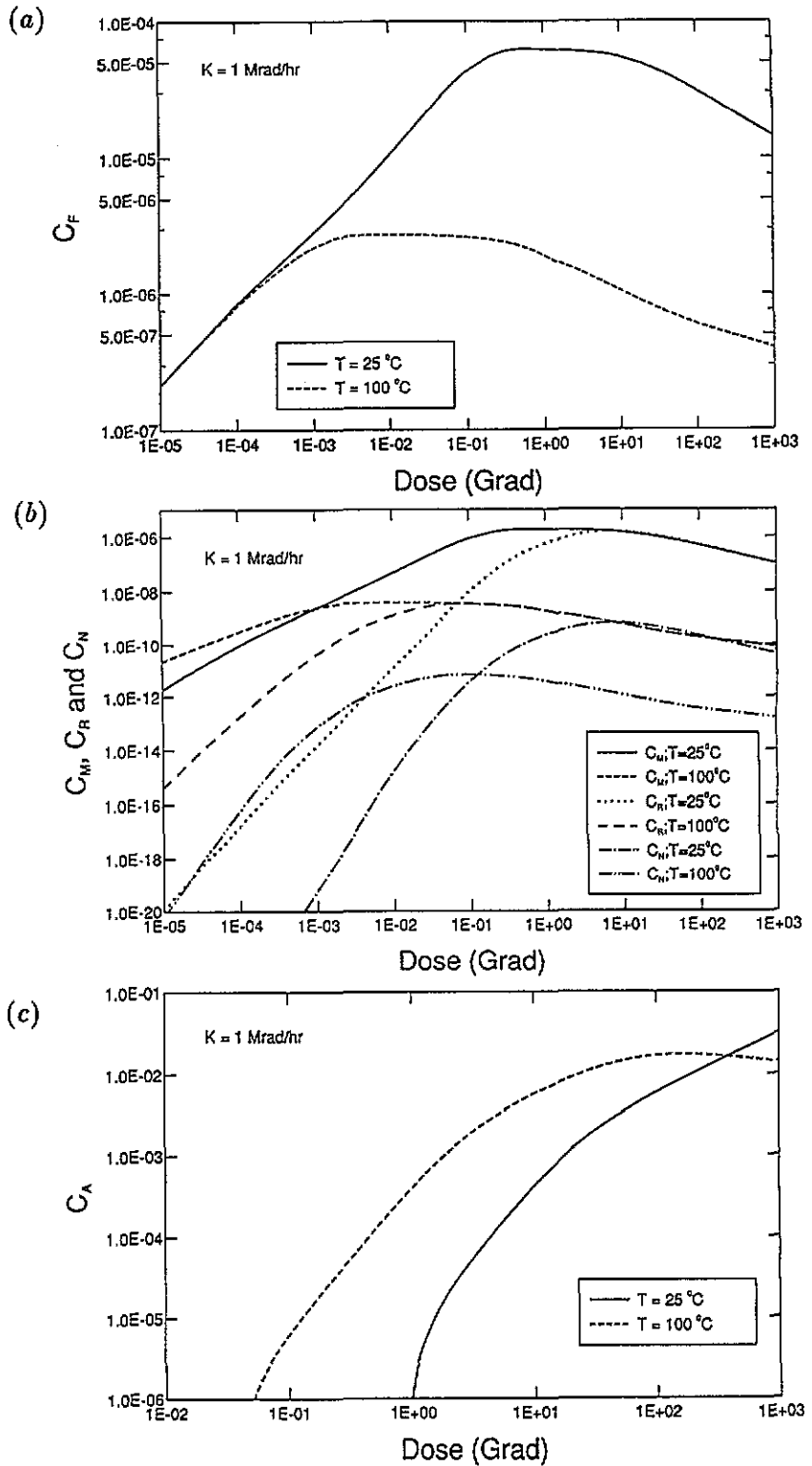
Figure 7. Defect concentration as a function of the dose: (*a*) F centres, (*b*) M, R and N centres, (*c*) colloids.

new F centres and the result is a net decrease of the F-centre concentration.

The behaviour of the concentrations of M, R and N centres is depicted in figure 7(*b*). The picture shows that for high doses and a given temperature, the concentrations of M and R centres approach the same value at high doses. Since the time derivative of c_R is proportional to $(c_M - c_R)$ (see equation (8)), c_R will increase until it equals c_M. As it is assumed that the colloid formation is energetically more favourable than the N-centre formation ($K_F > K_R$ in equation (9)), the concentration of the latter type of defects cannot reach the concentration of M and R centres and remains about two orders of magnitude smaller. It must be kept in mind though, that the results plotted in figure 7(*b*) will be qualitatively correct but quantitatively rather speculative due to a lack of experimental information on these defect centres.

The colloid formation, finally, starts after a certain threshold dose has been exceeded. This threshold depends on the temperature (see figure 7(*c*)) and the dose rate. The existence of such a threshold dose has been confirmed experimentally for NaCl crystals by Levy *et al* [24] and Hodgson *et al* [47]. These experiments have shown that this threshold is very sensitive to the density of dislocations prior to irradiation. This aspect will be discussed later in more detail. For higher temperatures, a saturation and even a decrease of the colloid concentration can be observed. This disintegration of the colloids starts when the dislocation sinks are saturated ($\rho_d = \rho_m$) and the newly created H centres increasingly recombine with colloids.

4.2. Variation of c_A with temperature and dose rate

The colloid fraction as a function of the temperature shows a bell shape (figure 8). As shown by Lidiard [8] the colloid fraction is in the low temperature limit proportional to $\sqrt{(D_F/K)}$. At higher temperatures, the evaporation of F centres from colloids and the recombination of F centres with molecular Cl_2 increases until, for a given dose rate, colloid formation is not possible at all. These reactions lead to a decrease of c_A. The result is that for a given dose rate and a given total dose, the fraction of colloids has a maximum at a certain temperature. The position of this maximum depends on the dose rate and slightly on the total dose. In addition we see that the maximum colloid fraction increases significantly with decreasing dose rates.

In comparison with the original Jain–Lidiard model, the new model predicts that the colloid growth is less sensitive to the dose rate. With the old model, the colloid fraction increased with by a factor four when the dose rate was decreased by a decade [9]; now this increase is not more than a factor of 1.5. This reduction of sensitivity is a result of the incorporation in the model of the nucleation stage of the colloids and is in agreement with experimental data [6].

In figure 9, model calculations of c_A as a function of the dose rate are plotted for four different temperatures. At very high dose rates, the efficiency of the colloid formation is very low since in this limiting case, the probability for F and H centres to survive direct recombination is almost equal to zero. Decreasing K leads to an increase of c_A until a maximum is reached at K_{max}. Thereafter, c_A drops relatively quickly to zero at $K_{cut-off}$. At this dose rate, the drain of F centres to the colloids equals the evaporation of F centres from the colloids and below this dose rate no colloid growth can occur. The positions of $K_{cut-off}$ and K_{max} of course depend on the temperature at which the irradiation takes place. In comparison with the original Jain–Lidiard model, the positions of $K_{cut-off}$ and K_{max} are shifted to higher dose rates (by a factor of approximately five) and the intensity of the low-temperature peaks is notably reduced.
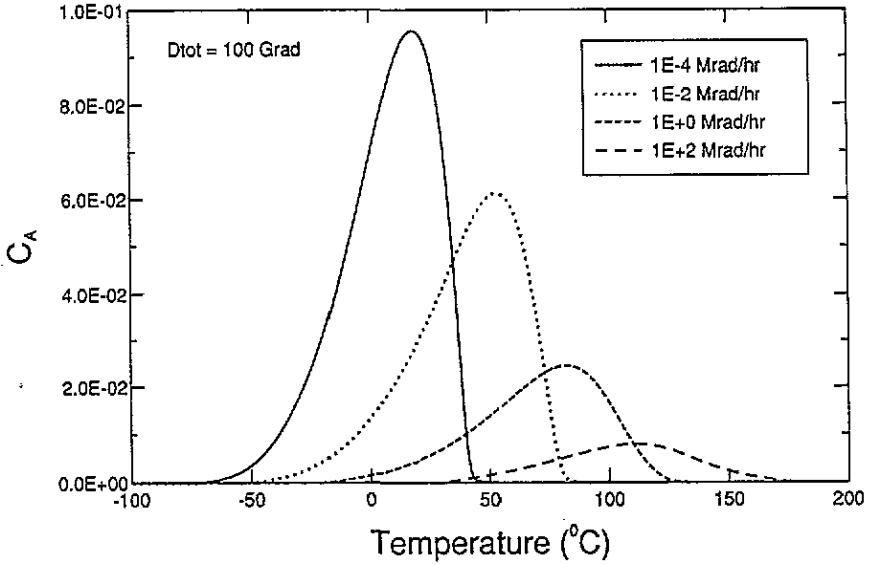
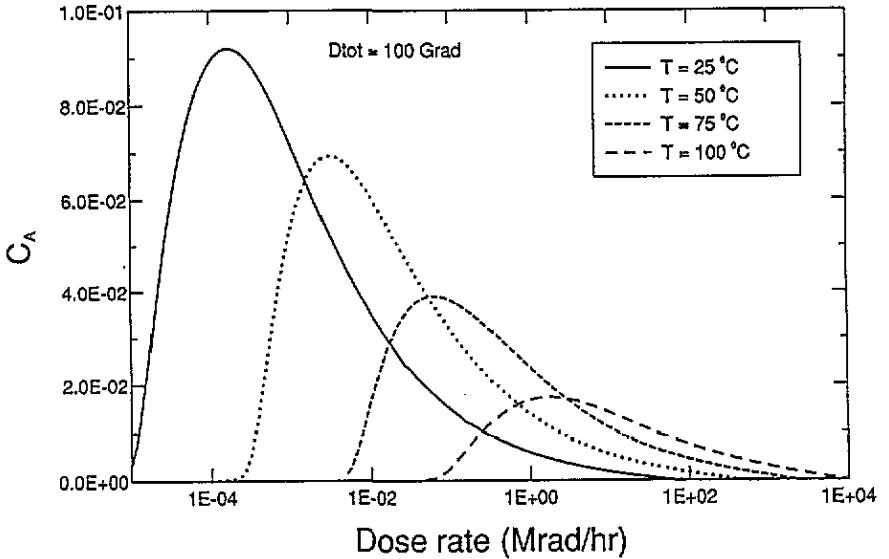**Figure 8.** Colloid fraction as a function of the temperature.

Figure 9. Colloid fraction as a function of the dose rate.

4.3. Impurities

A large number of experiments has shown that the radiation-induced F-centre concentration in alkali halides is considerably affected by the presence of impurities. In the present model this effect is incorporated by reactions which describe the trapping of H centres by impurities. Unfortunately, at present there are no systematic experimental data available on F-centre growth in NaCl doped with impurities. Almost all experimental effort on impurity-
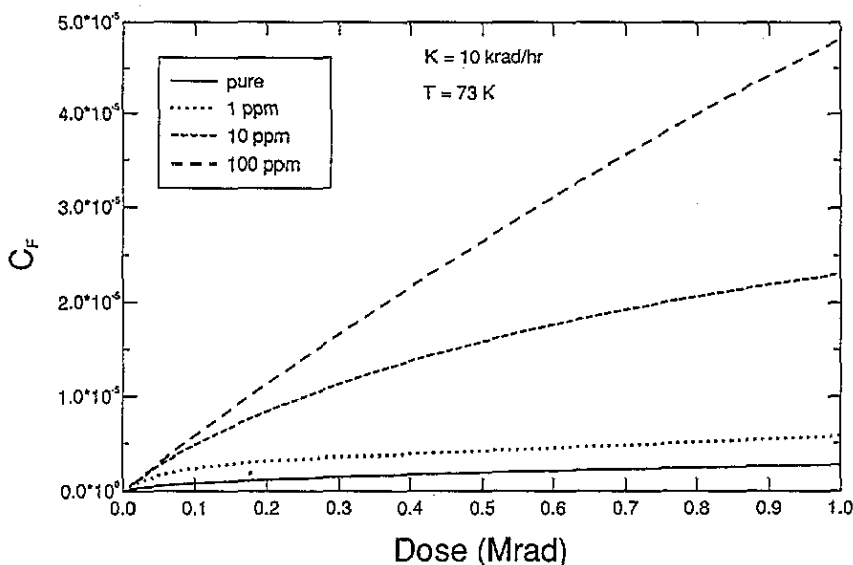
Figure 10. F-centre growth for various impurity concentrations.

related colour centre production has been concentrated on KCl crystals. Comparison of the model with experiments therefore has to be restricted to qualitative aspects. In figure 10, the F-centre growth curves at liquid nitrogen temperature for various concentrations of impurities are shown. The growth curves that appear agree quite well with experimental data on KCl doped with divalent impurities like Pb^{2+} [11]. Even the empirical relation between the F-centre concentration and the impurity concentration [15]:

$$c_F \propto \sqrt{c_{S_0}} \tag{23}$$

seems to hold. This empirical relation can be rationalized as follows [6]. In the beginning of an irradiation experiment, there will be a drain of H centres to impurity traps until the impurities are saturated. At this stage, equation (16) yields:

$$dc_{S_0}/dt = 0 \Rightarrow c_{S_1} = c_{S_0}c_H/c_{H,S_1}^{(e)} \tag{24}$$

and almost all F and H centres will recombine directly:

$$K = K_2 c_F c_H. \tag{25}$$

With the condition $c_F = c_H + c_{S_1}$, equations (24) and (25) lead to the following expression for the F-centre fraction at low doses.

$$c_F = \sqrt{(K/K_2)(1 + c_{S_0}/c_{H,S_1}^{(e)})}. \tag{26}$$

Thus for moderate temperatures (i.e. if the concentration of H centres in equilibrium with S_1 centres is much lower than the impurity concentration), the model confirms the empirical relation between the concentration of F centres and the concentration of impurities, as represented by equation (23).

As the dose is increased, c_F and c_H are dominated more and more by the drain of F and H centres to the colloids and the dislocation loops. In figure 11, C_c and C_l are plotted as a function of the temperature. The density of colloids has a maximum which is related
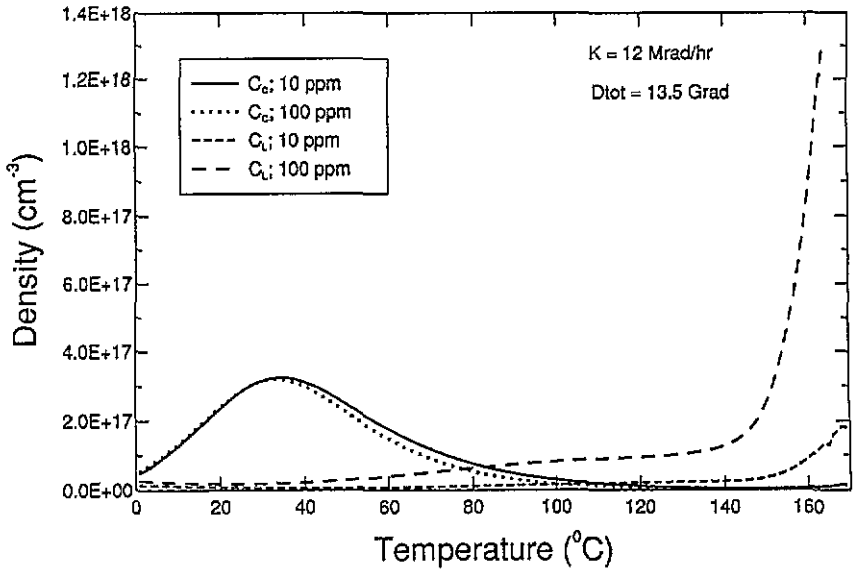
Figure 11. Number concentrations of colloids and dislocation loops versus the temperature.

to the maximum in c_N (see figure 7). Experiments confirm the existence of a maximum of C_c but indicate that it is located at a higher temperature [5]. Increasing the impurity concentration leads to a decrease of the colloid density since a reduction of c_H favours more the growth of colloids than the nucleation of colloids. The presence of impurities leads to a significant increase of C_l. From figure 11 we learn that this effect increases with increasing temperatures. Apparently the growth of S_3 centres, which are the beginnings of new dislocation loops, is more efficient at higher temperatures. Since the S_3 centres are considered to be thermally stable, the drain of H centres to the S_3 centres will increase at elevated temperatures because of the enhanced mobility of the former (see equation (14)).

In figure 12, the colloid fraction as a function of the temperature is shown for various concentrations of impurities. In this figure, we also show experimental data of Groote and Weerkamp [6] for this specific dose rate and total dose. These authors have studied the effect of various types of impurities in NaCl on radiation induced stored energy. The investigated dopants were Li, K, F, Br, Mn, Ba, Fe and KBF$_4$. In figure 12 the experimental data on K-doped NaCl are shown since doping with this impurity has yielded the largest differences in stored energy when compared with pure NaCl. The experimental data refer to NaCl, doped with nominally 1 mole% K and show about a doubling of the colloid fraction in comparison with pure NaCl (see figure 3). Groote and Weerkamp also reported that experiments with lower K impurity concentrations, down to 300 ppm, yielded the same results. This implies that the effect of impurities on c_A saturates for concentrations higher than approximately 100 ppm. Looking at the model predictions in figure 12, we see that the model is in good agreement with these experiments. According to the model, the colloid fraction increases with increasing impurity concentrations and the maximum of $c_A(T)$ shifts to lower temperatures. Both effects saturate for impurity concentrations higher than 100 ppm. It should be noted that the agreement between model and experiments is significantly better than for the model of Seinen *et al* [29].
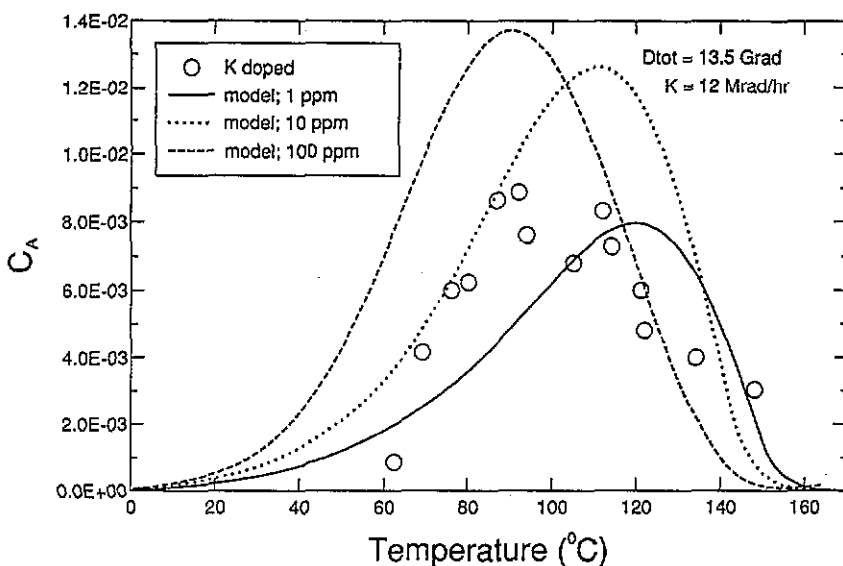
Figure 12. Model calculations of the colloid fraction compared with experimental data of Groote and Weerkamp on K-doped NaCl.

4.4. Strain

It is well established that colour centre formation in alkali halide crystals can be strongly influenced by subjecting the crystals to strain before irradiation. Experiments by Levy and coworkers [24] and by Durand *et al* [25] further showed that the precipitation of F centres into colloids increases with the dislocation density created by plastic deformation.

In the model there are two parameters that will depend on strain: ρ_0 and C_l^0. It appears that—according to the model—colloid growth is rather insensitive to ρ_0 for $\rho_0 < 10^{10}$ cm^{-2}. This insensitivity to ρ_0 has also been observed for the original Jain–Lidiard model [35]. It can be expected that, apart from the initial dislocation line density ρ_0, the number of nuclei for dislocation loops which will grow during irradiation, C_l^0, will also be increased when the crystal has been previously strained. In figure 13 the colloid fraction in the low-dose regime is shown for various values of C_l^0. It can be observed that increasing C_l^0 leads to a substantial reduction of the dose threshold for colloid growth. This effect levels off for C_l^0 larger than 10^{17} cm^{-3}. The threshold reduction and subsequent enhanced colloid growth agrees well with experiments. In figure 13 we also show experimental data by Levy *et al* [24] on pure NaCl crystals strained before irradiation. In order to translate the optical density data of these authors into colloid fractions, a conversion factor of 1 cm^{-1} OD $\equiv 4 \times 10^{-7}$ mole colloidal Na has been used. We see that once the threshold dose has been passed, the theoretical slope of c_A (approximately 2) agrees reasonably well with the experiments. In addition it can be noted that for NaCl crystals strained less than 10%, the model does not underestimate the colloid growth for $C_l^0 = 10^{15}$ cm^{-3}. This is a much better result than for the original Jain–Lidiard model [35]. Near the threshold dose, the experimental colloid fractions seem to be larger than predicted by the model but one should keep in mind that this region of c_A is on the edge of the experimental resolution. The experimental data for crystals strained to 10% before irradiation, however, show colloid fractions that are clearly larger than predicted by the model. In this case, one might question the validity of the model assumption that the colloids grow at a rate limited by bulk lattice diffusion of F
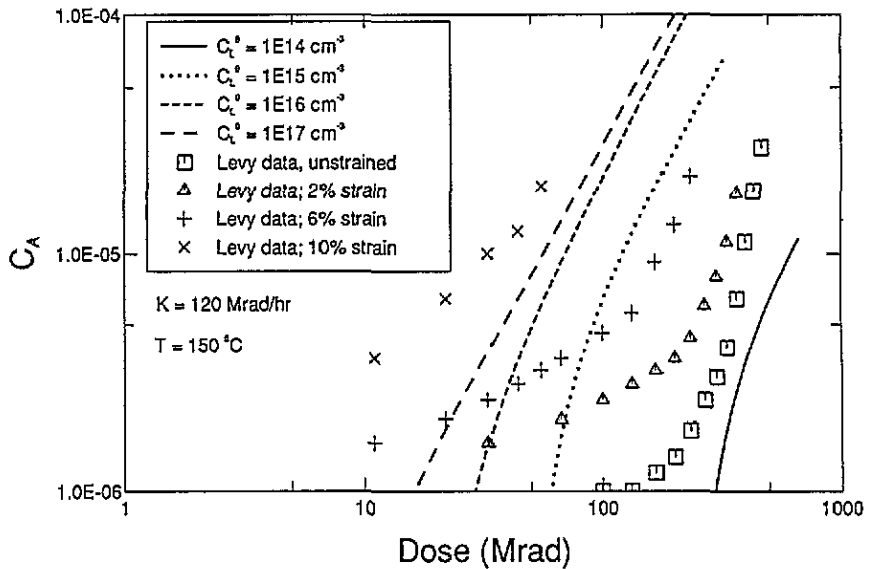
Figure 13. Colloid fraction in the low-dose regime. Model calculations with varying numbers of dislocation loop nuclei (C_1^0) are compared with experimental data of Levy *et al* on strained NaCl crystals.

centres. Hughes and Lidiard [35] have shown that, in crystals strained to 10% and more, colloid growth more likely occurs through dislocation 'pipe' diffusion of F centres.

5. Discussion and conclusions

The accumulation of radiation damage in rock salt is a complex process, involving a manifold of interactions between the various types of defects created by radiation. In order to meet with the practical demand for a theory describing the long-term behaviour of rock salt nuclear waste repositories several models have been developed and the nature of all these models is largely empirical. The model presented in this paper can be considered as the youngest member of this family of empirical models. Based on the Jain–Lidiard theory, it contains extensions which enable a better understanding of the role of the colloid nucleation stage and impurities in the formation of radiation damage in NaCl. Several experimental results, which were not covered by the original Jain–Lidiard model, are well described by the new model. The model extensions, however, are accompanied by some new parameters with a less solid experimental basis. For example, there is very little known about the equilibrium between the H centres and the S_1 and S_2 centres or about the stability of the N centres. These processes, fortunately, happen to have only a minor influence on the total process of radiation damage build-up. But there are also more fundamental mechanisms in the model which need more careful investigation.

Restricting ourselves to the colloidal formation, which is from a practical point of view the most important part of the radiation-damage process, the following model mechanisms are the most important.

(i) The efficiency of F–H pair production. In the model it is assumed that this efficiency is independent of the temperature, which seems reasonable, and independent of impurity

concentration and dislocation line density. These last two assumptions seem less evident. It is possible, though, that the impurity-induced change in the F–H pair production is well covered by the H-centre trapping process, incorporated in the model. It is not very likely, however, that an enhanced dislocation line density (as caused by strain) will not influence the decay of excitons and the subsequent F–H pair production.

(ii) The F centre diffusion coefficient. This parameter has not been determined very accurately yet but calculations with the present model and with older models indicate that the activation energy must be close to 0.8 eV.

(iii) The dislocation bias coefficient. Although there is substantial theoretical evidence that the mechanism of Hobbs is correct, implying that dislocation loop growth occurs because of H-centre aggregation near dislocation lines, there is little known about the actual preference of H centre drift with respect to F centre drift to dislocations. Jain and Lidiard have used a value for z_H which applied for metals but which, at the best, can only be a rough estimate for NaCl.

(iv) The colloid growth mechanism. In the model it is assumed that the colloid growth rate is controlled by bulk lattice diffusion of F centres. This is probably true for highly pure, single crystals but its validity for NaCl crystals with large amounts of impurities or dislocations can be questioned. Actually, Hughes and Jain have shown that, for heavily strained crystals, pipe diffusion of F centres is more probably the rate-limiting step in the colloid growth process.

(v) Back reaction between F centres and molecular Cl_2. In order for the model to accommodate experimental results of Jenks and Bopp, which showed a saturation of colloid growth at higher doses, Lidiard introduced this back reaction. This *ad hoc* mechanism satisfactorily helps to describe the high dose behaviour of the growth of colloids but still lacks a solid theoretical fundament.

Concluding this discussion, it will be clear that—although the model agrees very satisfactorily with experiments—more fundamental research on some basic model mechanisms is highly recommended.

Acknowledgments

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