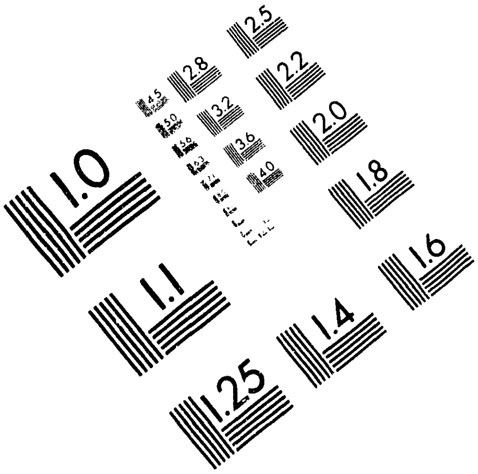

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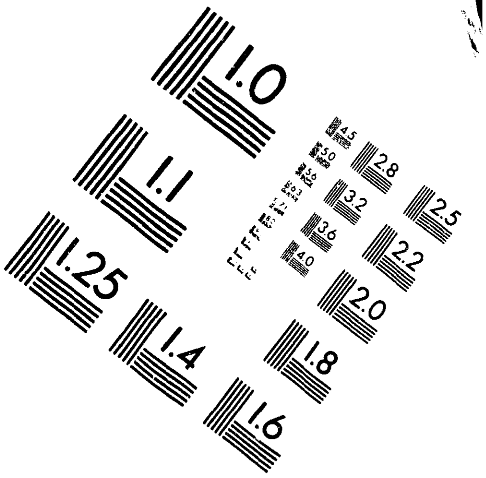

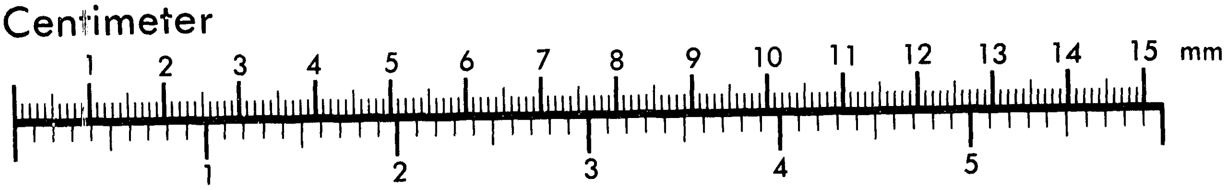

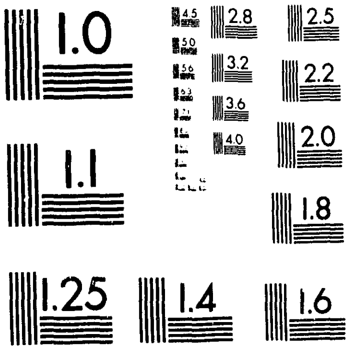

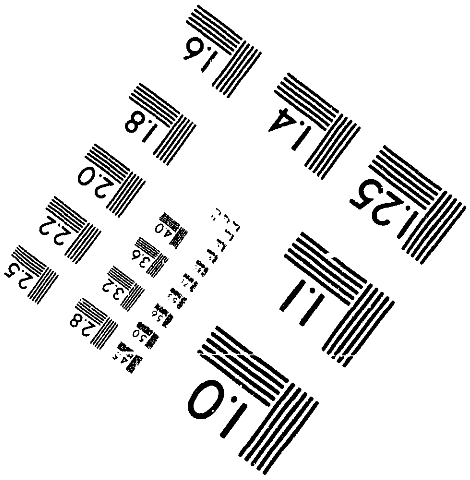

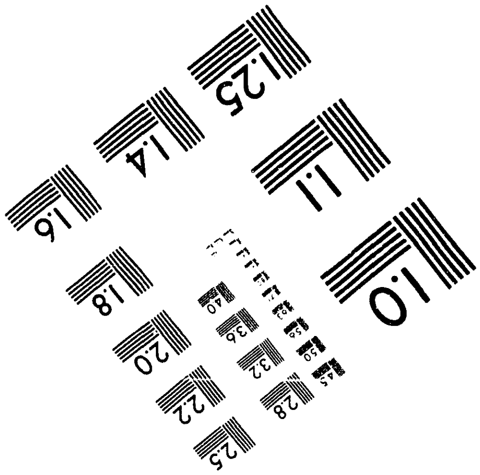

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THE LONG-TERM ALTERATION OF BOROSILICATE WASTE GLASSES

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THE LONG-TERM ALTERATION OF BOROSILICATE WASTE GLASSES

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Prediction of the long-term durability of glass waste forms under potential disposal conditions is based on a mechanistic model of glass corrosion which has been derived from short-term laboratory tests. The model of glass reaction that has evolved identifies the hydrolysis of an Si-O bond to release silicic acid as the step which controls the long-term glass reactivity [1-3]. This reaction step is initially fast under dilute solution conditions, but slows as the silicic acid concentration in solution increases. An increase in the solution concentrations of glass components will occur with progressive glass corrosion, and so the solutions which contact waste glasses over long reaction times will have high concentrations of glass components. Therefore, the glass reactivity is usually expected to decrease with the reaction progress as the contacting solution becomes more concentrated. The corrosion behavior of glasses contacted by highly concentrated solutions must be characterized to assess the long-term glass stability.

A commonly used method to attain high solution concentrations within short reaction times is to perform static leach tests at high glass surface area/leachant solution volume ratios (S/V). Under these conditions, very little glass must react to generate high solution concentrations. It has been suggested that short-term tests at high S/V may be equivalent to longer-term tests at low S/V and equivalent values of (S/V)t because the same solution concentrations are attained [4, 5]. Other work has shown that the different pH values attained in tests at different S/V may affect the reaction rate and must be accounted for when comparing the results of tests at equivalent (S/V)t [6-9]. In addition to the solution compositions, it must also be demonstrated that the glass alteration is equivalent in tests at different S/V to provide evidence that the corrosion mechanism is the same at different S/V, and that tests at high S/V can be utilized to characterize the long-term corrosion behavior of waste glass.

Recent hydrothermal leach tests of borosilicate glasses developed for vitrifying high-level waste at the Defense Waste Processing Facility (DWPF) have shown that the glass reactivity initially decreases as reaction products build up in solution, but then increases about ten-fold after secondary phases form [9,10]. Tests with other glass compositions have shown similar acceleration of the reaction when secondary phases form [11-13]. Acceleration of the reaction has been interpreted as an effect of secondary phase formation on the glass corrosion rate. Detailed analyses of reacted glasses are presented to compare the surface alteration in tests at different S/V conducted for different reaction times, both before and after the reaction is accelerated.

EXPERIMENTAL

A series of static leach tests has been conducted at S/V of 10 and 340 m^{-1} following a modified MCC-1 protocol [14] and at S/V of 2000 and 20,000 m^{-1} following a modified PCT protocol [15]. The results were used to compare the glass reactivity at different S/V for reaction times up to one year [9, 10]. Tests were conducted at 90°C in deionized water (DIW) or in tuff groundwater (EJ-13) using SRL 202 glass , which represents the initial glass composition to be produced by the DWPF [16]. The glass and EJ-13 compositions and the results from analysis of leachate solutions of tests through one year have been presented previously [9, 10, 17]. Results of solids analyses to compare the alteration of the SRL 202 glass surface at different S/V are presented here.

Reacted glass monoliths from the MCC-1 tests and reacted glass grains from the PCT tests were analyzed using analytical electron microscopy (AEM), which combines high resolution transmission electron microscopy with energy-dispersive x-ray spectroscopy (EDS). Representative samples of the reacted glass were fixed in epoxy and thin-sections prepared using an ultramicrotome . Grains of powdered glass were fixed in resin directly while sample chips were removed from reacted monoliths using a diamond knife. Secondary phases found distributed among the reacted grains were isolated and analyzed separately.

RESULTS

The AEM images of representative alteration layers that formed on SRL 202 glass in tests at S/V of 340 and 2000 m^{-1} are shown in Figure 1. The unreacted glass was chattered during sectioning, although the alteration layers were not chattered. Crystalline layers were observed to form at the glass surface in tests at all S/V and at all reaction times. Fibrous clay crystals formed oriented perpendicular to the glass surface at the shortest reaction times tested at all S/V (3 days in the PCT tests and 7 days in the MCC-1 tests). These became consolidated into laths of clay that were generally oriented perpendicular to the glass surface as the reaction continued. A mostly amorphous inner layer developed beneath the original crystalline layer in tests in DIW at longer times, with small, randomly oriented crystallites sometimes being distributed throughout the inner layer. Eventually, the inner layer crystallized into discrete laths oriented perpendicular to the surface and resulted in a twinned layer of crystalline laths. A mostly amorphous phase remained as a thin band

a. b.

c. d.

e. f.

Figure 1 High Resolution AEM Images of Alteration Layers Formed During the Reaction of SRL 202 Glass: a) 28 days/DIW, b) 360 days/DIW, and c) 360 days/EJ-13 at 340 m^{-1}, and d) 140 days/DIW, e) 360 days/DIW, and f) 360 days/EJ-13 at 2000 m^{-1}.

between the two crystallized layers in some samples.

Samples reacted in either DIW or EJ-13 at 20,000 m^{-1} for 364 days or longer acquired much thicker layers than samples reacted for shorter times. While the glass reacted for shorter times appeared visually unreacted, the glass reacted for 364 days or more was coated with a chalky white phase, which readily spalled from the glass. The layers formed in DIW at 20,000 m^{-1} after 182 and 364 days are shown in Figures 2a and 2b. The 182-day layer is similar to that formed after 360 days at 2000 m^{-1} (Figure 1e). The 364-day layer has two sublayers: an oriented outer layer and a thick inner layer. Figure 2c shows the unreacted glass/inner layer interface at a higher magnification. The glass is corroded unevenly and crystalline material persists to the interface. Figure 2d shows a relatively even interface between the oriented outer layer and the inner layer. Flocculated clay laths are seen at the surface of the outer layer.

Compositional analysis using EDS and structural analysis using selected area electron diffraction (SAD) showed that the outer and inner layers were composed of the same polycrystalline material, which is identified as a smectite clay. Table 1 gives a representative composition of the clay laths in the oriented outer layers and the random inner layer formed in DIW. The compositions of the inner and outer layers are similar; both are depleted of soluble glass components and enriched in aluminum and chloride. Clays with a similar composition are formed in EJ-13 [17]. Table 2 gives the lattice spacings measured using several representative SAD patterns and those of some smectite clays.

The structure and composition of isolated secondary phases were analyzed by AEM and SEM. Phases identified include the uranium-bearing phases weeksite and uranophane, chabazite and heulandite group zeolites, clinoptilolite, and nagelschmidtite. A noncrystalline feature bearing uranium and titanium was also identified within the clay phase or between the clay layer and the underlying glass. Detailed analyses of secondary phases will be presented elsewhere.

DISCUSSION

Many studies have shown that the S/V used in a test can be employed to accelerate the attainment of high solution concentrations of released glass components [4-10, 12]. The present tests show that 1) tests at high S/V also accelerate the alteration of the glass surface and the precipitation of other secondary phases from solution, 2) the layer thickness increases upon the generation of other secondary phases, and 3) the same alteration phase forms before and after the corrosion is accelerated (smectite clay), but its morphology changes. Similar layer structures are seen to form on glasses reacted at different S/V, although secondary phases develop faster in tests at higher S/V due to the higher solution concentrations. This implies that tests at low S/V can be used to characterize the initial glass reaction and tests at high S/V used to characterize the reaction in the presence of secondary phases.

The secondary phases are interpreted to affect the glass reaction rate through the solution chemistry, and their effect can be understood by considering the glass reaction mechanism. The glass reaction rate is usually expressed as the product of a rate coefficient (which depends on the intrinsic reactivity of the glass and the reaction temperature), and a reaction affinity term (which is a

a. b.

c. d.

Figure 2 High Resolution AEM Images of Alteration Layer Formed on SRL 202 Glass in Tests in DIW at 20,000 m^{-1}: a) after 182 days, b) after 364 days, c) High Magnification Image of Unreacted Glass/Inner Layer Interface, d) High Magnification Image of Oriented Outer Layer/Inner Layer Interface.

measure of the disequilibrium between the glass and the solution) [1-3]. The reaction affinity is expressed as the difference between the silicic acid concentration in solution and a "saturation" concentration that is unique for every glass composition, but is usually found to be similar to that of amorphous silica [2]. The glass reaction does not stop when silicic acid reaches the "saturation" concentration, rather the glass is continues to react at a low, constant rate. An *ad hoc* term is sometimes added to the analytical rate expression to account for experimental observations of continued reaction under saturated conditions [2, 18, 19].

As the glass dissolves, the solution may become saturated with respect to several stable secondary phases. If these phases form, they may equilibrate with the solution and control the solubility limits of some glass components. The

Table 1. Composition of Layers Formed on SRL 202 Glass Reacted in DIW at 20,000 m^{-1} for 364 Days*

Element	Outer Layer	Inner Layer	Unreacted Glass
Al	8.5	10	4.9
Ca	0.1	0.1	2.2
Cl	3.2	3.2	<0.5
Fe	20	16	21
K	0.6	0.9	7.5
Mg	1.1	1.5	0.2
Mn	4.4	4.7	4.3
Na	0.5	0.1	8.2
Ni	2.5	2.9	2.1
Si	57.8	59.5	48
Ti	1.3	1.1	1.6

*in elemental weight per cent, normalized to 100% total

Table 2. d-Spacings from Selected Area Electron Diffraction Analysis of SRL 202 Glass Reacted at 20,000 m^{-1} for 364 Days, in angstroms

Layer I	Layer II	Layer III	Nontronite (29-1497)*	Montmorillonite (12-219)	Saponite (29-1491)
			15.2	17.6	15.5
9.0**				9.00	
			7.44		7.73
				5.99	5.11
4.48	4.48	4.42±0.12***	4.48	4.49	4.57
		3.20±0.07	3.58	3.58	3.834
			3.05	2.99	3.07
2.57	2.53	2.58±0.05	2.564	2.57	2.61
				2.242	
		1.70±0.03		1.699	1.731
1.50	1.50	1.50±0.02	1.51	1.504	1.533
1.29	1.29	1.30±0.02	1.336	1.294	1.321

Layer I: outer layer/EJ-13; II: inner layer/DIW; III: outer layer/DIW

*JCPDS File number of representative smectite clay.

**Measured from lattice fringes in image.

***Estimated measurement errors common to all experimental values.

solution may be prevented from attaining "saturation" conditions in the presence of some secondary phases, and so the glass may continue to react at a high rate. If nucleation of these phases is delayed, the solution may become supersaturated with respect to the potential secondary phases and approach the "saturation" conditions of the glass. The glass reaction will be slow until the secondary phases precipitate, at which time the reaction will be accelerated. As long as a given assemblage of secondary phases controls the solution chemistry, the glass is expected to react at a constant rate. Under these conditions, the assemblage of secondary phases and their effects on the glass reaction rate must be known to project the long-term glass reactivity.

The reaction of borosilicate glasses can be described as proceeding in three stages: an initially high rate in dilute solutions, a decreasing rate in more concentrated solutions, and an increased rate after secondary phases form. The development of the alteration layers reflects the progress of the reaction through these stages. Layers formed initially consist of isolated crystallites, which develop into thicker laths as the solution becomes more concentrated. Both the glass corrosion and layer growth rates are low under high solution concentrations, and the layer may become well structured. After the glass corrosion accelerates, the layer crystallizes at a high rate, and so the crystals formed in the inner layer are smaller and more randomly oriented, in part, because they are not as readily accessible to the bulk solution as the outer layer. Continued reaction leads to an increase in the thickness of the inner layer, while the outer layer retains a nearly constant thickness.

Analyses of the reacted solids in these tests provide a partial compilation of the secondary phases formed as these particular glasses corrode. Further work is required to identify critical phases responsible for acceleration of the glass reaction. While most current reaction models identify the solution concentration of silicic acid as controlling the glass reaction rate, other glass components may also affect the rate. It is important to reach the stage of the glass reaction where secondary phases affect the reaction rate in performance tests because the reaction under these conditions represents the long-term reaction rate. The reaction rates observed prior to secondary phase formation may be much lower than those achieved after secondary phases precipitate. The effects of secondary phase formation on the glass reaction rate and the distribution of released radionuclides must be fully accounted for in performance assessments to reliably predict the long-term durability of waste forms.

ACKNOWLEDGMENTS

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REFERENCES

1. B. Grambow, "A General Rate Equation for Nuclear Waste Glass Corrosion," Mat. Res. Soc. Symp. Proc., 44, 15-24 (1985).
2. B. Grambow, "Geochemical Approach to Glass Dissolution," in Corrosion of Glass, Ceramics and Ceramic Superconductors: Principles, Testing, Characterization and Applications, D.E. Clark and B.K. Zoitos, eds., Noyes Publications, Park Ridge, NJ, pp124-152 (1991).
3. W.L. Bourcier, D.W. Peiffer, K.G. Knauss, K.D. McKeegan, and D.K. Smith, "A Kinetic Model for Borosilicate Glass Dissolution Based on the Dissolution Affinity

of a Surface Alteration Layer," Mat. Res. Soc. Symp. Proc., 176, 209-216 (1990).

4. L.R. Pederson, C.Q. Buckwalter, G.L. McVay, and B.L. Riddle, "Glass Surface Area to Solution Volume Ratio and its Implications to Accelerated Leach Testing," Mat. Res. Soc. Symp. Proc., 15, 47-54 (1983).

5. J.E. Mendel, compiler, "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," Pacific Northwest Laboratory Report PNL-5157 (1984).

6. P. van Iseghem, W. Timmermans, and R. DeBatist, "Parametric Study of the Corrosion Behavior in Static Distilled Water of Simulated European High-Level Waste Glasses," Mat. Res. Soc. Symp. Proc., 44, 55-62 (1985).

7. E. Vernaz, T. Advocat, and J.L. Dussossoy, "Effects of the SA/V Ratio on the Long-Term Corrosion Kinetics of R7T7 Glass," Nuclear Waste Management III, 175-185 (1990).

8. W.L. Ebert, "The Effects of the Leachate pH and (Glass Surface Area/Leachant Volume) on Glass Reaction," Phys. Chem. Glasses (in press).

9. W.L. Ebert and J.K. Bates, "Comparison of Glass Reaction at High and Low SA/V," Proceedings of the Third International Conference of High-Level Radioactive Waste Management, Vol 1, Las Vegas, NV, pp. 934-942 (1992).

10. J.K. Bates, W.L. Ebert, X. Feng, and W.L. Bourcier, "Issues Affecting the Prediction of Glass Reactivity in an Unsaturated Environment," J. Nucl. Mater., 190, 198-227 (1992).

11. C.C. Allen, D.L. Lane, R.G. Johnston, A.D. Marcy, and R.R. Adee, "Hydrothermal Studies of Simulated Defense Waste Glass Plus Basalt," Mat. Res. Soc. Symp. Proc., 44, 451-458 (1985).

12. J. Patyn, P. Van Iseghem, and W. Timmermans, "The Long-Term Corrosion and Modeling of Two Simulated Belgian Reference High-Level Waste Glasses-Part II," Mat. Res. Soc. Symp. Proc., 176, 299-307 (1990).

13. B. Grambow and W. Lutze, "Performance Assessment of Glass as a Long-Term Barrier to the Release of Radionuclides into the Environment," Mat. Res. Soc. Symp. Proc., 112, 713-724 (1988).

14. U.S. Department of Energy, "Nuclear Waste Materials Handbook" DOE/TIC-11400 (1982).

15. C.M. Jantzen and N.E. Bibler, "The Product Consistency Test for the DWPF Wasteform," Westinghouse Savannah River Report WSRC-MS-90-149 (1990).

16. J.R. Fowler and M.J. Plodinec, "Projected Compositions and Radiogenic Properties of DWPF Glasses," Proc. of Third International High-Level Radioactive Waste Management (IHLRWM) Conference, Las Vegas, NV, Apr. 12-16, 1992, pp 904-910 (1992).

17. W.L Ebert, J.K. Bates, E.C. Buck, and C.R. Bradley, "Accelerated Glass Reaction Under PCT Conditions," Mat. Res. Soc. Symp. Proc. (in press).

18. B. Grambow and D.M. Strachan, "A Comparison of the Performance of Nuclear Waste Glass by Modeling", Pacific Northwest Laboratory Report PNL-6698 (1988).

19. D.M. Strachan, B.P. McGrail, M.J. Apted, D.W. Engle, and P.W. Eslinger, "Preliminary Assessment of the Controlled Release of Radionuclides from Waste Packages Containing Borosilicate Waste Glass, " Pacific National Laboratory Report PNL-7591 (1990).

Fig 1a

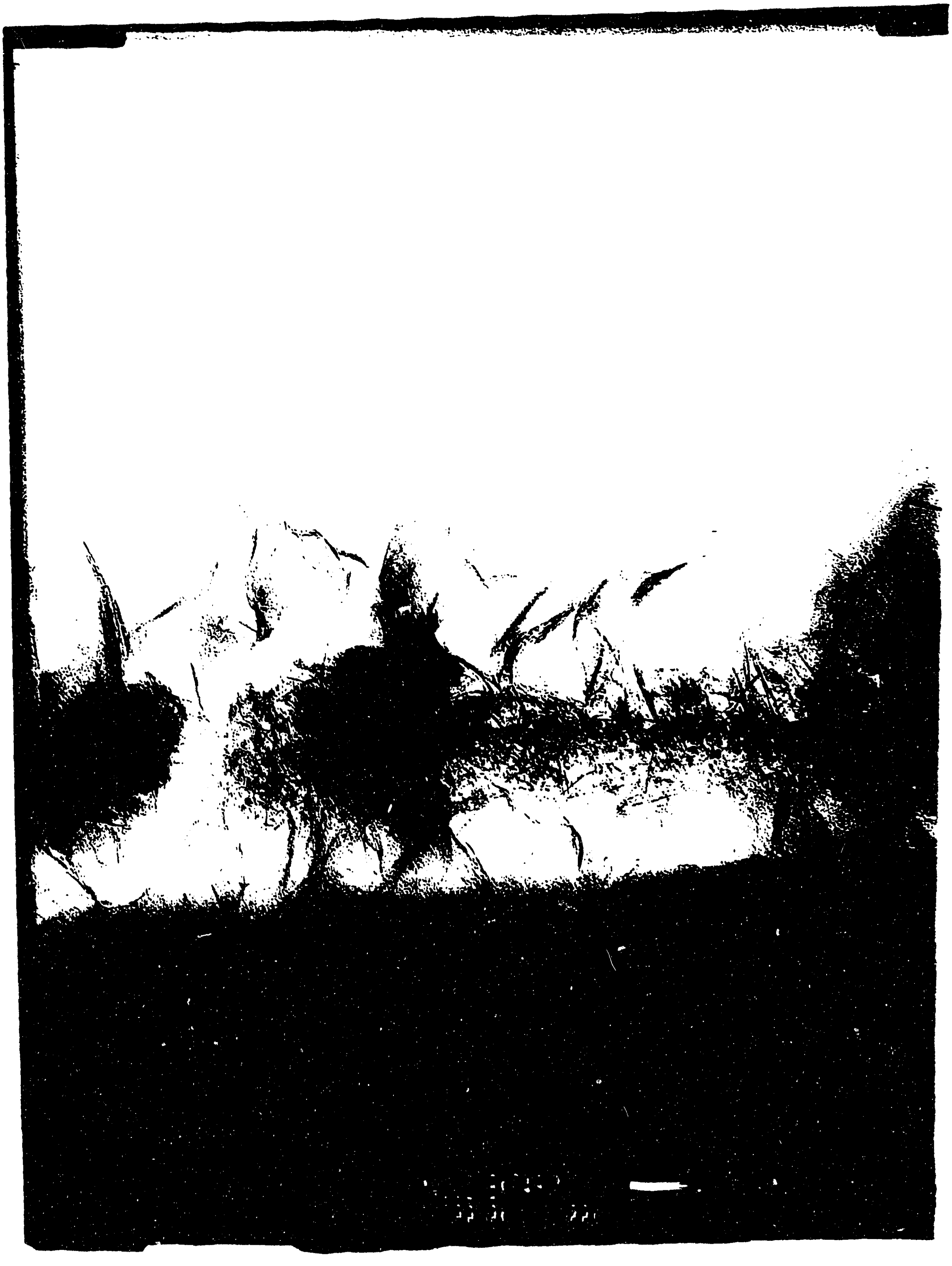

Fig. 16

Fig 1c

Fig 1d

Fig 1e

Fig 1f

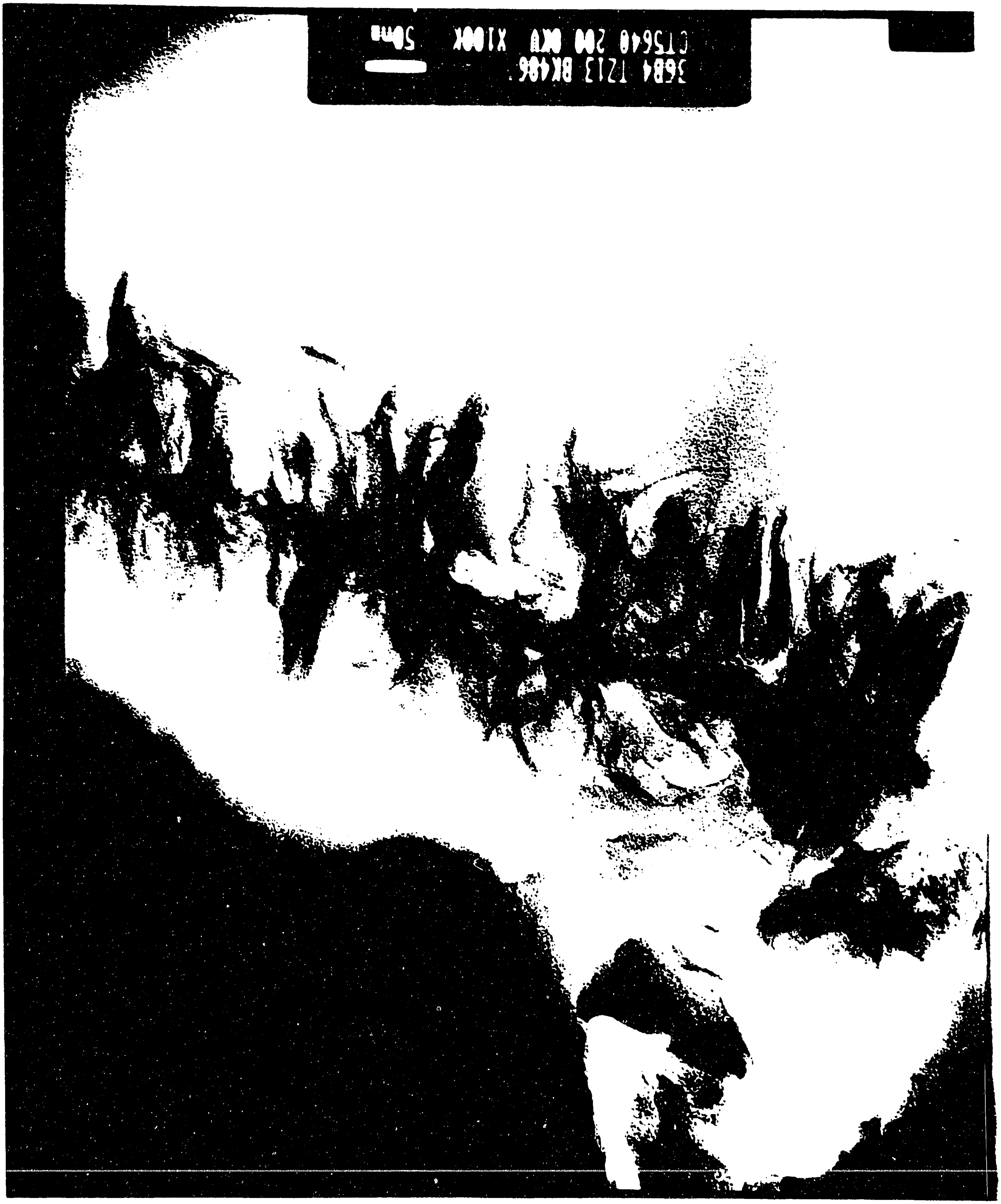

Fig 7,2

Fig 7.b

Fig 2d

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