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DEVELOPMENT AND VALIDATION OF KEY AEROSOL MODELS FOR SOURCE TERM PREDICTIONS IN SODIUM-COOLED FAST REACTORS DURING BEYOND DESIGN BASIS ACCIDENTS

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Abstract

During Sodium-cooled Fast Reactors (SFRs) severe accidents, it is foreseen that material in the form of liquid sodium mixed with fuel and fission products would be ejected into the containment. In the presence of oxygen, combustion of sodium (Na) results in the conversion of a large fraction of the burnt Na into Na-oxide aerosols that would govern the suspended radioactivity inside the containment; this together with the potential harm associated with the chemical species resulting from the Na-oxides reaction with water vapour present in the atmosphere would be responsible to a great extent for the radiological and chemical impact of any potential source term. In this sense, the characterization and behaviour of Na-based aerosols generated during in-containment Na-fires is of fundamental importance for the assessment of the radiological consequences in SFR severe accidents.

The work in this thesis presents a step forward in modelling in-containment source term during potential severe accidents in Na-cooled reactors. A phenomenological model for sodium-oxide particle generation during sodium pool-fires has been developed (PG model). The model covers sodium-vapour evaporation from a sodium pool and formation of sodium-oxide aerosols and calculates the characteristics (number and size) of the particulate source term to the containment. It consists of a suite of individual models for Na vaporization (diffusion layer approach), O₂ transport by air natural circulation (3D flow pattern modelling to capture the associated turbulence foreseen right above the reaction region), Na-O₂ chemical reactions (instantaneous reactions and energy of reaction) and vapour-to-particle conversion of Na-oxides (i.e., nucleation and/or condensation). A partial validation with available experimental data showed a consistent model response in terms of burning rates. As using 3D computational fluid dynamics in analysis of Beyond Design Basis Accidents at present is unsuitable (lack of validated SFRs severe accident tools) and impractical (expensive computer resources), a zero-D (lumped) approach has been developed. Subsequently the model has been adapted to be implemented in the severe-accident computer code ASTEC-Na CPA by transposing the PG formulation into a form with those specific variables included in the code. The performance of the ASTEC-Na CPA with the proposed correlations implemented has been tested against some of the more sound available data in the open literature. In conclusion, the new correlations derived from the PG model are very suitable for use in a severe-accident code in terms of the negligible additional computational burden. The new correlations, by originating from simplifications of soundly-based physical modelling, avoid the arbitrary assumption of a fixed primary-particle size in the existing modelling. Limited comparisons with

experiments imply that use of the new correlations increases confidence in prediction of the pool-fire particulate source term to the containment.

The work performed in this thesis is framed in the CIEMAT contribution to the JASMIN project from the 7th Framework Programme of the European Commission (contract number 295803).

Sinopsis

En el transcurso de un accidente severo en un reactor rápido refrigerado por sodio (SFR), se prevé la expulsión a contención de material en forma de sodio líquido mezclado con combustible y productos de fisión. En presencia de oxígeno, la combustión del sodio da lugar a la conversión de una gran fracción del sodio consumido en aerosoles que gobernarán la radioactividad suspendida en contención; este hecho junto con el daño potencial asociado a las especies químicas resultantes de la reacción de los óxidos de sodio con el vapor de agua presente en la atmósfera serán los responsables en gran medida del impacto radiológico y químico de cualquier posible término fuente. En este sentido, la caracterización y el comportamiento de los aerosoles provenientes del sodio generados durante fuegos en la contención es de suma importancia para la evaluación de las consecuencias radiológicas de los accidentes severos en los SFRs.

Esta tesis representa un avance en el modelado del término fuente en contención en el caso de un hipotético accidente severo en un SFR. Para ello, se ha desarrollado un modelo fenomenológico para la generación de partículas de óxido de sodio durante un fuego tipo piscina de sodio (modelo PG). El modelo engloba la evaporación de sodio desde la piscina y la formación de los aerosoles de óxido de sodio y calcula las características (número y tamaño) de las partículas que componen el término fuente en contención. El modelo consiste en un conjunto de modelos individuales para la vaporización del sodio (aproximación de capa difusiva), transporte del O_2 mediante circulación natural de aire (patrón de flujo 3D para capturar la turbulencia asociada prevista justo encima de la región de reacción), reacciones químicas $Na-O_2$ (reacción instantánea y energía de reacción) y conversión vapor-partícula de los óxidos de sodio (es decir, nucleación y/o condensación). Su validación parcial frente a datos experimentales ha mostrado una respuesta consistente en términos de tasa de quemado. La utilización de cálculos 3D fluido-dinámicos en accidentes más allá de la base de diseño resulta actualmente inapropiado (falta de herramientas validadas) y poco factible (costosos recursos informáticos). Por ello, se ha desarrollado una aproximación cero-D (parámetros concentrados). Posteriormente, el modelo ha sido adaptado para su implementación en el código de accidente severo ASTEC-Na CPA. La actuación del nuevo código resultante de la implementación de las correlaciones propuestas ha sido examinada mediante la comparación con los datos más consistentes disponibles en la bibliografía publicada. Como conclusión, las nuevas correlaciones derivadas del modelo PG resultan muy adecuadas para su utilización en códigos de accidente severo en términos de la insignificante carga computacional que añaden. Las nuevas correlaciones, al originarse a partir de simplificaciones de modelos físicos sólidos, evitan la suposición arbitraria de un

tamaño fijo de partícula primaria presente en los modelos actuales. Las comparaciones con experimentos, aunque limitadas, dejan ver que el uso de las nuevas correlaciones aumenta la confianza en las predicciones del término fuente en contención resultante de incendios de piscinas de sodio.

El trabajo realizado para esta tesis se ha llevado a cabo en la unidad de investigación en seguridad nuclear del CIEMAT como parte del proyecto internacional JASMIN perteneciente al 7th Programa Marco de la Comisión Europea (número de contrato 295803).

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Chapter 1

INTRODUCTION

Sodium-cooled Fast Reactors (SFRs) are one of the six technologies considered in the so-called Generation IV (Gen. IV) initiative. A full-scope safety analysis of this reactor type would need to have computation tools developed and properly validated. Potential sodium discharge in the containment during postulated Beyond Design Basis Accidents (BDBAs) would have major consequences for accident development in terms of energetics and source term. In the containment, sodium vaporization and subsequent oxidation would result in supersaturated oxide vapours that would undergo rapid nucleation creating toxic aerosols. Therefore, modelling this vapour nucleation is essential to proper source term assessment in SFRs. This thesis is a contribution to the technical understanding of the in-containment source term during postulated severe accident scenarios in sodium-cooled fast reactors. It is focused on the development of a phenomenological particle generation model to calculate the particle generation rate and their primary size during an in-containment sodium pool fire.

This section introduces the scenario, the background and the frame of this work. A brief overview of Sodium-cooled Fast Reactors (SFRs) history and technology is also given.

1.1. SFRs: overview

The SFR uses liquid sodium as the reactor coolant. It features a closed fuel cycle for fuel breeding and/or actinide management. Owing to the significant past experience accumulated with SFRs in several countries, the deployment of SFR systems is targeted for 2030.

Plant size options under consideration range from small, 50-300 MWe modular reactors to large plants up to 1500 MWe. The sodium outlet temperature from the core is 500 – 550°C for all the options.

Important safety features of the SFR system include a long thermal response time (high thermal inertia), a reasonable temperature margin to coolant boiling, a primary system that operates near atmospheric pressure and an intermediate sodium system between the radioactive sodium in the primary system and the power conversion system. Furthermore, the fast neutron spectrum greatly extends existing uranium resources compared to thermal reactors.

Both water/steam (Rankine cycle) and supercritical carbon dioxide or nitrogen (Brayton cycle) are being considered for the power-conversion system to achieve high thermal efficiencies, safety and reliability.

1.1.1. A short history of SFR development

The evolution of fast reactors dates back to the early prototypes in the 50s. More than ten experimental fast reactors and eight prototype and commercial size fast reactor plants have been constructed and operated (Table 1).

The first operational fast reactor, Clementine, was constructed in USA. It became critical in 1946. The first kilowatt-hour of nuclear electricity in history was produced in December 1951 by a fast reactor, the EBR-I in Idaho (Fig. 1).

Fig. 1. Light bulbs energized by electricity from EBR-I (December 20, 1951) (IAEA, 2012).

In the 1960s and 1970s, the US programme continued R&D and construction of fast reactors of increasing power: EBR-II, FERMI and Fast Flux Test Facility (FFTF). Several experimental SFRs were also built and operated successfully in the former Soviet Union (BR-5/BR-10, BOR-60), the UK (Dounreay Fast Reactor, DFR) and France (RAPSODIE).

A few years later, Germany and Japan started national development programmes and constructed experimental fast reactors, KNK and JOYO, respectively.

At this point experimental reactors were operating in many countries providing R&D tools for various prototype and commercial sized fast reactor development programmes. The fast reactor development reached a peak around 1980. Phénix and Superphénix in France, SNR-300 in Germany, Monju in Japan, PFR in the UK, Clinch River Breeder Reactor (CRBR) in the USA or BN-350 and BN-600 in USSR are examples of that.

However, during the next ten years the fast reactor development was progressively slowed down, presumably because of the commercial success of Light Water Reactors (LWRs). By 1994, the CRBR was cancelled and the FFTF and EBR-II shut down in USA. In France, Superphénix was shut down at the end of 1998; SNR-300 in Germany, although completed, was never put into operation; KNK-II was shut down in 1991. In the UK, PFR was shut down in 1994 and BN-350 in 1998.

Today, renewed interest in nuclear power has highlighted the medium and long term benefits of fast reactors with a closed fuel cycle. New energy demands arise in developing countries such as China and India, whereas global warming due to the use of fossil fuels and the growing disposal problem of radioactive wastes from LWR spent fuel became major issues.

New programmes are underway in China with the China Experimental Fast Reactor (CEFR), connected to the grid in July 2011, India with the construction of the Prototype Fast Breeder Reactor (PFBR) or Russia with the operation of the BN-800 reactor. In France, the Gen. IV SFR prototype project called ASTRID is ongoing. The Republic of Korea and Japan proceed in their design of KALIMER-600 and the Japanese Sodium-cooled Fast Reactor (JSFR), respectively (Pioro, 2016).

Table 1. Sodium fast reactors in the world.

	Reactor	Type	Country	Thermal power (MW)	Criticality	Status
Experimental	CLEMENTINE (Hg)		USA	0.02 MW _{th}	1946	A: 1952
	EBR I (NaK)	Loop	USA	1.4 MW _{th}	1951	A: 1963
	BR 1		USSR	0.03 MW _{th}	1955	A
	BR 2 (Hg)		USSR	0.2 MW _{th}	1956	A: 1957
	BR 5 - BR 10	Loop	USSR	5/10 MW _{th}	1958/1973	A: 2002
	DFR (NaK)	Loop	UK	75 MW _{th}	1959	A: 1977
	LAMPRE		USA	1 MW _{th}	1961	A: 1965
	EBR II	Pool	USA	60 MW _{th}	1963	A: 1994
	RAPSODIE	Loop	France	24/40 MW _{th}	1967/1970	A: 1983
	BOR 60	Loop	USSR	60 MW _{th}	1968	F
	SEFOR	Loop	USA	20 MW _{th}	1969	A: 1972
	KNK I - KNK II	Loop	Germany	60 MW _{th}	1972/1977	A: 1991
	JOYO	Loop	Japan	50 MW _{th}	1977	A: 2007
	FFTF	Loop	USA	400 MW _{th}	1980	A: 1994
	FBTR	Loop	India	40 MW _{th}	1985	F
	PEC	Loop	Italy	120 MW _{th}		A: 1987
	CEFR	Pool	China	60 MW _{th}	2010	F

	Reactor	Type	Country	Thermal power (MW)	Criticality	Status
Demonstrators	FERMI	Loop	USA	100 MW _e	1963	A: 1972
	BN 350	Loop	Kazakhstan	150 MW _e	1972	A: 1998
	PHÉNIX	Pool	France	250 MW _e	1973	A: 2009
	PFR	Pool	UK	250 MW _e	1974	A: 1994
	SNR 300	Loop	Germany	300 MW _e		A: 1992
	MONJU	Loop	Japan	280 MW _e	1992	A: 2010
	CRBR	Loop	USA	350 MW _e		Ab: 1983
	KALIMER	Pool	Korea	150 MW _e	2025	P
Power	BN 600	Pool	USSR	600 MW _e	1980	F
	SUPERPHÉNIX	Pool	France	1200 MW _e	1985	A: 1998
	BN 800	Pool	USSR	800 MW _e	2014	F
	SNR 2	Loop	Germany	1400 MW _e		Ab
	CDFR	Pool	UK	1300 MW _e		Ab
	EFR		Europe	1500 MW _e		Ab
	PRISM	Pool	USA	1245 MW _e		Ab
	JFSR	Loop	Japan	1500 MW _e	2025	P
	KALIMER-600	Pool	Korea	600 MW _e	2025	P
	PFBR	Pool	India	500 MW _e	2010	Constr.

A: Shutdown; F: Operating; P: Project; Ab: Abandoned

1.1.2. Current framework

In this context, in May 2001, the Generation IV International Forum (GIF) (https://www.gen-4.org/gif/jcms/c_9260/public) arose as an international collaboration among 13 countries to face the challenges of developing the next generation of nuclear power plants. It first established the development goals of Gen. IV reactors (GIF, 2002):

- Sustainability: generating sustainable energy and promoting long term availability of nuclear fuel by optimizing the use of the fuel till the 96% of the energy utilization; minimizing nuclear waste and reducing the long term stewardship burden.
- Safety and reliability: imposing enhanced safety design options like passive systems for very low likelihood and degree of reactor core damage and eliminating the need for offsite emergency response.
- Proliferation resistance and physical protection: providing increased physical protection.
- Economics: having a life cycle cost advantage over other energy sources and offering a level of financial risk comparable to other energy projects.

Generation IV (Gen. IV) designs are striving to reach the highest safety standards ever applied to Nuclear Power Plants (NPPs). Accidents with significant fuel damage (i.e., severe accidents) are being considered in the design phase so that they can be inherently avoided or prevented and/or mitigated by passive design features or by ad-hoc engineering safeguards with elimination of the need for offsite emergency response. This enlargement of design scope with respect to Gen. II and Gen. III reactors is a challenge for all the technologies involved in the systems chosen for Gen. IV since accident scenarios involve complex phenomena that have to be taken into account when demonstrating reactor safety.

In 2003, the GIF announced the selection of 6 reactor technologies which they believe represent the future shape of nuclear energy (Table 2):

- Very High Temperature Reactor (VHTR)
- Gas-cooled Fast Reactor (GFR)
- Sodium-cooled Fast Reactor (SFR)
- Lead-cooled Fast Reactor (LFR)
- Molten-Salt Reactor (MSR)
- Super-Critical Water-cooled Reactor (SCWR)

Among them, Sodium-cooled Fast Reactors (SFRs) is more mature than other Gen. IV designs since several SFR have been operated (cf. Table 1, above) and, as a result, the experience that has been gained currently amounts to > 400 operational years.

SFRs operate with high-energy neutrons which greatly extends the use of uranium resources compared to thermal reactors. The SFR is designed for management of high-level wastes and, in particular, management of plutonium and other actinides. The focus was to utilize uranium resources by using plutonium which is generated by transmutation of ^{238}U during operation of a reactor. Due to the higher effectiveness of fast neutrons for fissioning actinides, SFRs hold a leading role in the actinide management. SFRs incorporate numerous features that create a less-challenging safety environment: a low pressure system with a long thermal response time, a large temperature gap to coolant boiling and negative power and temperature coefficients. However, in the event of sodium boiling (or entrainment of a gas bubble through the core), the Achilles' heel of SFR technology is a positive void coefficient for the core, i.e., local increase in reactivity if liquid sodium is replaced by vapour or gas. However, the core design for ASTRID shows ways to minimize this effect (Varaine et al., 2012).

Table 2. Overview of Gen. IV systems (Pioro, 2016).

System	Neutron spectrum	Coolant	Outlet temperature (C)	Fuel cycle	Size (MWe)
VHTR	Thermal	Helium	900-1000	Open	250-300
GFR	Fast	Helium	850	Closed	1200
SFR	Fast	Sodium	500-550	Closed	50-150 300-1500 600-1500
LFR	Fast	Lead	480-570	Closed	20-180 300-1200 600-1000
MSR	Thermal/Fast	Fluoride salts	700-800	Closed	1000
SCWR	Thermal/Fast	Water	510-625	Open/Closed	300-700 1000-1500

1.1.3. SFRs technology

Sodium properties

Sodium is an alkaline metal with high atomic mass number. The atomic structure of sodium represents a single electron in its outer orbit, which accounts for its strong chemical activity. At room temperature it is a soft, silvery and highly reactive metal and is also ductile.

The good neutronic properties enable sodium to be an excellent coolant for fast reactors. Sodium has little slowing effect on neutrons produced by fission, it does not change fast spectrum properties and it has low capturing power (small cross section). Furthermore, sodium has a low level of activation (nuclear quality sodium) where the major radioactive isotopes generated by neutron capture are ^{24}Na ($t_{1/2} = 15$ h) and ^{22}Na ($t_{1/2} = 2.58$ y).

Because of the absence of moderator, the core is generally small and the power density, i.e., the power per unit volume, is high. This makes it essential to use a coolant with good thermal properties. At atmospheric pressure, sodium is in liquid state from 371 K to 1156 K. Sodium has very good thermal conductivity and reasonable specific heat capacity (Table 3). In addition to its good heat transfer characteristics, liquid sodium has exceptional thermal stability up to high temperatures. Low vapour pressure of sodium results in a high boiling point under atmospheric pressure. Sodium has a low viscosity and density (Table 3). Therefore, in the event of loss of primary pumping, a natural circulation capability is assured with the high thermal conductivity, the high system temperature and the large temperature gradient between the core inlet and outlet coolant (400 to 550° C).

But in spite of its very attractive safety characteristics, sodium exhibits potentially dangerous properties that must be considered, i.e. sodium reacts violently when it comes in contact with air or water, producing hydrogen and heat. Measures for sodium fires and sodium-water reaction should be taken into account in the system design.

Table 3. Thermophysical properties of sodium (Fink and Leibowitz, 1995).

Properties	Values
Atomic mass	22.989 g/mol
Melting point	371 K
Boiling point	1156 K
Vapour pressure	$1.80 \cdot 10^{-10}$ MPa (400 K)
Density	919 kg/m ³ (400 K)
Viscosity	$371 \cdot 10^{-4}$ Pa s (371 K)
Thermal conductivity (liquid)	87.22 W/m · K (400 K)
Specific heat	28.23 J/mol · K
Heat of vaporization	96.96 kJ/mol

Basic description of a plant

The core is accommodated in the reactor vessel which generally includes a vessel and a plug. Sodium in the vessel has a liquid level just below the vessel head and is covered by inert gas (argon generally) to control the vessel pressure by dampening variations. Some plants adopt guard or safety vessels outside of reactor vessels that can maintain the sodium level in case of primary sodium leak. In other designs, an in-vessel core catcher is foreseen to collect, contain and cool the molten core material following a severe accident and prevent it from escaping the containment building. The plug is required to have functions of thermal insulation and shielding against high operation temperature and high neutron flux. On the plug, an upper core structure is installed and provides control rod driver line guides and support for core instrumentations. The control rods are inserted from above the core by gravity or other acceleration devices.

Typical core configuration consists of core fuel, control rods, blanket (breeder) fuel and shields. The core fuel is a mixture of plutonium and depleted uranium. The blanket fuel is depleted uranium. Two chemical forms of fuel elements exist: oxide and metal (mixed uranium-plutonium-zirconium metal alloy). Burnups in the range of 150-200 GWD/MTHM have been experimentally demonstrated for both. Nevertheless, the databases for oxide fuels are considerably more extensive than those for metal fuels. The neutron absorber used in control rods is boron carbide (B_4C).

In the core fuel region, fissile nuclides such as ^{239}Pu and ^{241}Pu undergo fission to produce energy and excess neutrons. In the core and blanket fuel regions, fertile nuclides such as ^{238}U and ^{240}Pu contribute to the fissile nuclides breeding by capturing excess neutrons.

The core distribution can be homogeneous or heterogeneous (axial/radial). In the former (Fig. 2), the fuel region is surrounded by axial and radial blanket fuels for an efficient neutrons capture. In most cases, the outer core fuel has higher plutonium enrichment than that of inner core to flatten the radial power distribution. In the later, fertile blanket fuels are used in the core fuel region (Fig. 2.1b and 2.1c). With this configuration the neutron leakage from the core to the internal blanket fuel region is enhanced which yield higher breeding ratios and reduced sodium void reactivity, but it requires higher fissile fuel inventories.

Fig. 2. Typical SFR core configurations: (a) homogeneous core, (b) axial heterogeneous core and (c) radial heterogeneous core (Pioro, 2016).

The core fuel element or fuel pin contains the core fuel, upper and lower axial blanket fuels and the fission gas plenum within a cladding tube. The fuel pins are assembled as a fuel element bundle in a hexagonal assembly duct (wrapper tube) to form the fuel assembly of fuel subassembly. The cladding and wrapper tubes are made of high-strength stainless steels.

The fuel elements are separated by a spiral wrapping wire or grid spacers in which the sodium coolant flows. The fuel elements are placed in a tight triangular lattice

arrangement to maximize the fuel volume fraction for core neutron performances and to minimize the core size for the plant capital cost reduction (Fig. 3).

Fig. 3. Typical SFR core fuel element and fuel assembly (Handbook Piero 2016).

The cooling system is at low pressure and high temperature and includes a primary and an intermediate sodium systems as well as secondary water-steam systems (gas secondary systems have been proposed for some designs).

Currently, there are two design options for the SFR plant: loop and pool type. In the pool type (left hand layout, Fig. 4), the reactor core, primary pumps and intermediate heat exchangers (IHXs) are immersed in a large pool of sodium in the reactor vessel. Sodium is discharged from the IHX to the pool, is eventually drawn to the pump inlet, is forced upward through the core and re-enters the heat exchanger. In the loop type (right hand layout, Fig. 4), the primary coolant circulates through the primary heat exchangers located outside of the reactor pressure vessel. Primary sodium coolant enters toward the bottom of the vessel, flows upward through the core and exits to the IHX. The intermediate loop then carries the heat energy to the steam generator. Advantages of the pool type are large thermal inertia and primary sodium contained by a simple vessel. On the other hand, those of the loop type are a compact reactor vessel/structure with better seismic resistance.

Both configurations employ multiple primary and intermediate coolant circuits to divide the heat load and provide redundant backup capability in the event of component

failures. They are also configured to enhance natural-convection circulation. The intermediate system transfers the heat from the IHXs to the steam generator unit during power operation. It represent a barrier between the radioactive primary sodium system and the non-radioactive water/steam system.

Several steam generator designs are employed for SFR systems: once-through and U-tube units (SNR-300, PFR or CDFR systems), once-through steam generators with helical tubes (Phénix and Superphénix systems) or “hockey stick” design with bent tubes (CRFR system). The high temperature steam is used to drive a conventional turbine that produces the electricity.

Fig. 4. Pool/loop type concepts layout.

A Beyond Design Basis Accident (BDBA) in a SFR can be initiated in the core by a variety of reasons, and, although unlikely, it may propagate inside the primary system, first as a shock wave, second as a sodium momentum and third as an expanding gas bubble (Fistedis, 1972). There is even a non-zero probability that some sodium may escape from the primary system so the containment should offer leak-tightness and structural adequacy for the temperatures and pressures generated by sodium fires outside the primary system and prevent dispersion of radioactive materials to the environment if these postulated events would occur.

Four types of containment systems are found in the literature review (NEA-CSNI, 1979). The upper part of the single containment accommodates a low-leakage rate; the Fast

Flux Test Facility (FFTF) is an example of this type of configuration. The double containment is a sealed, inerted high-pressure inner containment barrier that is surrounded by a low-leakage outer containment building. The containment type is a sealed, low-leakage inner containment barrier, surrounded by a ventilated low-pressure outer confinement building with discharge to stack via an air-cleaning system; the Superphénix reactor is an example. Finally, the multiple-containment is a sealed, high-pressure inner containment barrier, surrounded by one or more outer barriers; a negative pressure zone is maintained in the outermost space by pumping back leakages to the inner containment space. In this design, eventual venting to the stack via the air-cleaning system is provided. The German SNR-300 reactor was supposed to have this containment type. Fig. 5 shows sketches of the four types of containment designs.

Single containment system

Double containment system

Containment of the Superphénix

Containment of the SNR-300

Fig. 5. Containment types.

1.2. BDBAs in SFRs

During hypothetical, very low probability SFR accidents leading to severe core damage, one can envisage highly energetic phenomena in the vessel, i.e., a sodium vapour explosion, leading to ejection of sodium mixed with fuel, fission products, steel and cover gas from primary system into the containment. Indeed, despite their very low probability, it is a requirement of level 2 probabilistic safety assessments that such events are analysed and, ultimately, the associated source term evaluated (i.e., proving above all, significant mitigation with respect to public health and safety).

A SFR severe accident implies the disruption of the core by supercriticality involving more or less violent rupture of fuel pins and destruction of certain number of fuel assemblies (Fischer and Wright, 1984; Kayser and Papin, 1998; Klickman et al., 1982; Wright et al., 1985). Subsequently the interaction between hot fuel and liquid sodium can lead to a vapour explosion which could create a breach in the primary system (Powers et al., 2010; Tobita et al., 2006). Some primary sodium would be ejected into the containment building where this sodium would oxidize and burn. This sodium would be contaminated with components from disrupted fuel as well as activated.

During a severe accident, the phenomenology in the primary system is at every stage very complex. The initial event is absence of liquid-sodium cooling in some zone on the core. Such a situation may arise due to a number of combined elements where a classic scenario is long-term absence of forced circulation with failure of shut-down systems (Unprotected Loss Of Flow scenario, ULOF). This will lead to heat up of primary sodium to boiling. From this point, the accident evolves rapidly. In the supercritical dried-out zone, very fast neutronic overheating of the fuel occurs up to its rupture, with the subsequent release of the gaseous and volatile fission product inventory. The thermal and neutronic energy generated by the disruption is propagated to neighbouring fuel assemblies causing a rapid dry-out and disruption event that can potentially affect the whole core (Core Disruptive Accident, CDA). Projection of the hot debris from the core then could create a sodium-vapour explosion. After Fuel-Coolant Interaction (FCI), a foaming and expanding mixture of liquid and vaporized sodium, core debris, vaporized fuel components and gases (fuel-pin filler gas and fission gases) form an expanding bubble which mechanically uplifts the overlying sodium that then impacts on the reactor vessel head and could potentially cause a breach (Fig. 6) or ejection of sodium through vessel head penetrations.

Fig. 6. Expanding gas bubble representation.

In this scenario, contamination from the core can reach the containment either as vapours and aerosols transported through the sodium by bubbles or, if absorbed into the

liquid sodium, as vapours by evaporation into the cover-gas space. Under accident conditions, aerosols form essentially by three processes:

- vaporization of core materials and subsequent re-condensation where this would happen mainly in the primary-system where sodium and such particles would be largely retained in the primary sodium;
- coolant vaporization and subsequent re-condensation (Na-aerosols) where this would happen mainly in the primary system and such particles would be partly retained in the primary system and the leak path to the containment;
- ejection of sodium into air where burning occurs producing sodium-oxide aerosols that continue to react with the humidity and carbon dioxide of the air (so-called aerosol ageing) creating, in general, aerosols of mixed composition, i.e., Na_2O_2 - NaOH - Na_2CO_3 - NaHCO_3 .

The largest source of aerosols in the containment arises from burning of ejected sodium and condensation of the combustion products. Given the large amount of sodium inventory in a SFR primary system (about 2000 tonnes in a ~ 1500 MWe pool-type SFR, according to IAEA (2006)), one of the key accident variables is the total amount of sodium entering the containment. The importance of the sodium aerosols lays in their abundance and nature as both a radioactive source and a radioactive species carrier, and the potential harm associated with some of the chemical species (i.e., the effects of exposure to sodium oxide and hydroxide aerosols, depending on the level of exposure, can vary from mild irritation to burns, pneumonitis and serious damage to the upper respiratory tract). In addition, the total amount of aerosols in the containment strongly affects the source term evolution within the containment (Ferlandjian, 1985).

In the general case, sodium combustion produces aerosols initially composed of both sodium oxide and sodium peroxide. Very high aerosol concentrations can arise in the containment due to combustion, as much as $> 10 \text{ g m}^{-3}$. The subsequent evolving, mixed speciation of these aerosols depends on the kinetics of the ejection event given that aerosols that form early in the accident will have more opportunity to react with the air and reach the bicarbonate form; for later aerosols, reacting gases (i.e., H_2O and CO_2) may become depleted or vanish and little or no change to these later aerosols would occur. Nevertheless, with such high aerosol concentrations, agglomeration will be significant tending over time to render the overall composition of individual aerosols more uniform.

1.3. Background

During hypothetical SFR accidents leading to severe core damage, the ejection of material in the form of liquid sodium mixed with fuel and fission products from the primary circuit into the containment can be foreseen. A consequence assessment of this low-probability scenario requires knowledge of the major aerosol properties and evolution under the anticipated conditions within the containment, i.e., a proper evaluation of the in-containment source term.

In the frame of the CP-ESFR project (7th Framework Programme of the European Commission, contract number 232658), CIEMAT has participated with the main objective of building up Phenomena Identification and Ranking Tables (PIRT) on the fission product and aerosol generation and transport within a generic SFR containment during postulated BDBAs. To do that, an exhaustive review of currently available data and modelling capabilities of in-containment source term analysis in accident conditions was done.

1.3.1. Some basics of aerosol physics

Most relevant processes for “sodium-based” aerosols can be generally described by expressions found in the common aerosol literature (Davies, 1966; Loyalka, 1976; Pertmer and Loyalka, 1978, 1977). As a consequence, sodium aerosol evolution can be well described by the General Dynamic Equation (GDE) of aerosols, as proposed by Pertmer and Loyalka (1977),

$$\begin{aligned} \frac{\partial}{\partial t} n(r, t) = & \frac{1}{2} \int_0^r \phi(s, r-s) \cdot n(s, t) \cdot n(r-s, t) \cdot ds - n(r, t) \int_0^\infty \phi(r, s) \cdot n(s, t) \cdot ds \\ & - \frac{\partial}{\partial r} n(r, t) \cdot \frac{\partial r}{\partial t} - n(r, t) \cdot R(r, t) + S(r, t) \end{aligned} \quad (1)$$

which describes the evolution over time, t , of the number concentration, n , of particles with size r . On the right-hand side of the GDE the different terms are: the first two arise from particle agglomeration (addition and removal of particles with size r), the third one corresponds to vapour condensation onto particles, the fourth one encapsulates all the particle removal mechanisms and the last one is the source term. Major reviews of aerosol dynamics exists (e.g., Davies, 1966; Fuchs and Sutugin, 1969; Seinfeld and Pandis, 2006). A brief discussion of major aerosol mechanisms is listed below.

The process referred to as agglomeration or coagulation describes what happens when two or more particles collide due to a relative motion between them, stick to each other and form a larger particle. The net result is a continuous decrease in number concentration coupled with an increase in particle size (Hinds, 1999). Four agglomeration processes are treated in current severe accident codes: Brownian diffusion, differential gravitational settling, and turbulent agglomeration by shear and inertial forces.

Brownian agglomeration results from the random motion of particles suspended in a gas, caused by collisions with gas molecules. This movement gives rise to diffusion of particles in a concentration gradient analogous to gas diffusion and it is most significant for small particles where the free molecular regime and transition regime must be considered.

The gravitational agglomeration is based on the difference in sedimentation rates for particles of different sizes that results in situations where one particle overtakes another. Particles falling under the influence of gravity will distribute themselves over a range of speeds because of the dependence of the resistance of air on particle size. As a result, coarse particles will tend to sweep past finer ones, thereby causing collisions.

The collision frequency between particles suspended in a gaseous medium may be substantially increased by turbulent motion of the gas. This increase in collisions between particles may be the result of two independent mechanisms acting on the aerosol. The first mechanism produces collisions between particles of all sizes in a given distribution. The collisions occur because of turbulent eddies carry particles across streamlines to contact other particles (turbulent shear agglomeration). The second mechanism (turbulent inertial agglomeration) arises from the difference in density between the turbulent fluid and the suspended particles so that particles of various sizes have different response times, i.e. the inertia of a droplet depends on its size. This process will not give collisions between droplets of equal sizes.

Only the discussed agglomeration rate are included in current aerosol behaviour models but additional mechanisms can exist such as those resulting from centrifugal forces, laminar flow fields, electrical fields, magnetic fields, diffusing gas or temperature gradients.

The condensation onto or evaporation of a vapour from aerosols are considered in GDE. The condensation and evaporation may take place on aerosols, an either process can occur simultaneously with condensation or evaporation from heat sink surfaces.

In the removal term, the deposition mechanisms are included. Deposition occurs through a number of processes, including gravitational settling, diffusion to surfaces,

thermophoresis and diffusiophoresis. Of these natural depletion processes, gravitational settling is often the dominant mechanism, although phoretic effects may be significant in some cases. In general, particle diffusion is considered to be a relatively unimportant deposition process

Gravitational settling is the deposition of particles onto available floor or horizontal areas by gravity. Sedimentation is generally the most effective deposition process

Diffusion of particles to the internal surfaces of the enclosure takes place in the form of Brown's movement in the concentration gradient on the surface. It is mainly relevant for small particles.

Thermophoresis is a Brownian process causing migration of particles toward lower temperatures. Particles suspended in a gas experience a force directed toward cooler temperatures if the gas exhibits a temperature gradient; this force results from the interaction between gas molecules and the particles.

And finally, diffusiophoresis is the deposition induced by condensation of water vapour onto surfaces. When water condenses on (evaporates from) a structure surface, composition gradients will exist in the adjacent gas which will affect aerosol deposition in the surface due to two related effects. The first is that there will be a net molar flux of gas toward (away from) the condensing (evaporating) surface, and this net flux, commonly called the Stefan flow will tend to move aerosol particles with it. The second effect is that differences in the momentum transferred by molecular impacts on opposite sides of the particle will tend to drive the particle in the direction of decreasing concentration of the heavier constituent. In a strict sense, only this second component constitutes diffusiophoresis; however, the term "diffusiophoresis" commonly includes both effects.

1.3.2. State-Of the Art on in-containment source term

Aerosol characterization and size distribution

The characterization and behaviour of in-containment nuclear aerosols is of fundamental importance for assessing the radiological consequences of reactor accidents and for setting up filtering systems and even reactor components. A number of experimental studies have been conducted to physically and chemically characterize Na compounds in aerosols. Some of the most outstanding facilities involved in this investigation are: CSTF in U.S. (Hilliard et al., 1985; Postma and Owen, 1980; Souto et al., 1994), FAUNA in Germany (Cherdron and Charpenel, 1985; Cherdron and Jordan, 1980),

ATF in India (Subramanian et al., 2009; Subramanian and Baskaran, 2007), NSPP in U.S. (Adams et al., 1979) and ESMERALDA in France (Jordan et al., 1988).

Sodium fires resulting from accidental releases of liquid sodium from a SFR would produce aerosols consisting of sodium oxides which would react with available water vapour and carbon dioxide in the air. The exposure of these sodium oxide aerosols (Na_2O and Na_2O_2) to humid air results first in the formation of sodium hydroxide (NaOH) (forming solution droplets if water vapour is abundant). The NaOH particles thus formed would be particularly corrosive and hazardous (as are the oxides). Reaction of hydroxide with carbon dioxide to form the carbonate (Na_2CO_3) would make the aerosol substantially less chemically hazardous (Cooper, 1980). Formation of the bicarbonate almost renders the aerosols completely chemically innocuous.

Table 5 and **¡Error! No se encuentra el origen de la referencia.** (Casselman, 2009; Cooper, 1980) gather some physical constants of sodium compounds and the relevant reactions of sodium with oxygen, water and carbon dioxide and, respectively.

Table 4. Some physical constants for sodium compounds.

Name	Formula	Density (g/cm ³)	Melting Point (°C)	Boiling Point (°C)
Sodium monoxide	Na_2O	2.27	1132	1950
Sodium hydroxide	NaOH	2.13	318	1388
Sodium peroxide	Na_2O_2	2.80	675	decomp.
Sodium carbonate	Na_2CO_3	2.53	851	1600
Sodium superoxide	NaO_2	2.20	551	decomp.

Table 5. Relevant reactions of sodium and their compounds.

Sodium combustion	
$2\text{Na} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{Na}_2\text{O}$	$\Delta H_{298}^0 = -100.7 \text{ kcal/mole}$
$2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$	$\Delta H_{298}^0 = -120.6 \text{ kcal/mole}$
Chemical reactions in open atmosphere	
$\text{Na} + \text{H}_2\text{O(l)} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2$	$\Delta H_{298}^0 = -33.7 \text{ kcal/mole}$
$\text{Na} + \text{H}_2\text{O(g)} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2$	$\Delta H_{298}^0 = -45.7 \text{ kcal/mole}$
$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$	$\Delta H_{298}^0 = -46.8 \text{ kcal/mole}$
$2\text{Na} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{O} + \text{H}_2$	
$\text{Na} + \text{NaOH} \rightarrow \text{Na}_2\text{O} + \frac{1}{2}\text{H}_2$	$\Delta H_{298}^0 = 1.59 \text{ kcal/mole}$
$\text{Na} + \frac{1}{2}\text{H}_2 \rightarrow \text{NaH}$	$\Delta H_{298}^0 = -13.7 \text{ kcal/mole}$
$\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \frac{1}{2}\text{O}_2$	$\Delta H_{298}^0 = -124.0 \text{ kcal/mole}$
Sodium-concrete interaction	
$2\text{Na} + \text{CO}_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3$	$\Delta H_{298}^0 = -175.3 \text{ kcal/mole}$
$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	$\Delta H_{298}^0 = -40.0 \text{ kcal/mole}$
$\text{NaOH} + \frac{1}{2}\text{CaO}_3 \rightarrow \frac{1}{2}\text{Na}_2\text{CO}_3 + \left[\frac{1}{2}\text{Ca(OH)}_2 \rightarrow \frac{1}{2}\text{CaO} + \frac{1}{2}\text{H}_2\text{O} \right]$	
$4\text{Na} + \text{CaCO}_3 \rightarrow 2\text{Na}_2\text{O} + \text{CaO} + \text{C}$	
$4\text{Na} + 3\text{SiO}_2 \rightarrow 2\text{Na}_2\text{SiO}_3 + \text{Si}$	
$2\text{NaOH} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$	

Most of the experimental studies conducted have focused on the timing of Na-oxide aerosols transformation to hydroxide ones (NaOH) and, subsequently, to carbonates (Na_2CO_3) in a range of conditions varying, in particular, relative humidity (Cherdron et al., 1985; Hofmann et al., 1979; Subramanian et al., 2009). Essentially, all studies agree that transformation to NaOH is a fast process of the order of 1 to tens of seconds, depending on the conditions (Hofmann et al., 1979). According to data available, the formation of carbonates is nearly complete after hundreds of seconds as long as the relative humidity is appreciable, e.g., over 260 s at RH above 20% (Cherdron et al., 1985), and within 500 s at RH between 50 to 65% (Subramanian et al., 2009); at low RH such transformation has been measured to be much slower. Fig. 7 illustrates the carbonate formation kinetics according to Cherdron et al. (1985). Cherdron et al. explained the carbonate formation kinetics based on the concepts of saturation of solution and on-particle condensation.

Fig. 7. Carbonate formation in sodium fire aerosols.

The above observations were supported by theoretical studies (Clough and Garland, 1971; Cooper, 1980). These are both based on gas-phase transport theory and in-particle diffusion; in other words, they assumed that chemical reactions are much faster than physical transport of reacting gases. By comparing with data from Hofmann et al. (1979), Cooper found a noticeable consistency of his predictions. Table 6 summarizes the

characteristic time determined by Cooper as a function of the particle size. However, analysis and experimental work by Mathé et al. (2015) showed that an assumption in the Cooper model leads to conversion rates to sodium carbonate that are several orders of magnitude too fast. The authors proposed a modified Cooper model which they partially validated on their own experiments.

Table 6. Characteristic time (s) of mass transport processes for different particle size.

Mechanism	0.1 μm	1.0 μm	10 μm
Diffusion within a reacting droplet	1×10^{-6}	1×10^{-4}	1×10^{-2}
Gas-phase transport of H_2O	6×10^{-6}	3×10^{-4}	3×10^{-2}
Diffusion of H_2O within a Na_2O_2 agglomerate	-	1×10^{-3}	1×10^{-1}
Gas-phase transport of CO_2	2×10^{-4}	1×10^{-2}	1
Diffusion of CO_2 within a NaOH agglomerate	-	1×10^{-1}	1×10^{-1}
Diffusion within a reacting solid particle	1×10^{-2}	1	1×10^{-2}

Most of the experimental data available till 1980 were gathered in NEA-CSNI (1979). As noted in Table 7 (NEA-CSNI, 1979, Appendix B), the primary-particle size of nuclear fuel and coolant aerosols were reported in terms of geometrical diameter. At first sight, diameters of UO_2 and mixed $\text{UO}_2\text{-PuO}_2$ particles ranged from 0.003 to 0.1 μm ; sodium oxide particles were larger, ranging from 0.1 to 0.5 μm diameter; and mixed fuel and sodium produced particles of a size similar to sodium oxide alone (NEA-CSNI, 1979, Chapter II).

Table 7. Primary particle size measured by various investigations.

Reference	Material	Primary particle diameter, μm
Allent & Briant	Mixed UO_2 , PuO_2	Log-normal, bimodal, ($\sigma_g=1.35$) 0.003-.01
Chatfield	Pu , Na	0.02 maximum
Castleman	Mixed UO_2 , PuO_2	Log-normal, 0.004-.004, $\sigma_g=2.0$
	PuO_2	0.1, ($\sigma_g=1.9$)
	UO_2 , Na	0.2-0.6
Morrison et al.	Clad & bare UO_2	0.002-0.1
Kelly et al.	UO_2	<0.005-0.02
Jordan et al.	UO_2	$d_g=0.073$ ($\sigma_g=1.85$)
Kres	UO_2 , U_3O_8	0.014-0.034
Kitani	U_3O_8	$d_g=0.037$ ($\sigma_g=1.6-2.2$)
	U_3O_8	$d_g=0.07$ ($\sigma_g=1.93$)
Schikarski	Clad mixed Oxide fuel	<0.08
	Na_2O	0.1-0.4
Hilliard et al.	Na_2O_2 , NaOH	0.1-0.5
Parker et al.	UO_2 , U_3O_8	$d_g=0.034$

Several later studies indicated that the “initial particle size” of aerosols generated during a sodium fire in terms of Aerodynamic Mass Median Diameter (AMMD), was around $1 \mu\text{m}$ ($0.9 \mu\text{m}$ according to Cherdron et al. (1985) and $1.0 \mu\text{m}$ according to Jordan et al. (1988)). More recent investigations (Subramanian and Baskaran, 2007) measured AMMDs around $1.2 \mu\text{m}$ in the temperature range $250-550^\circ\text{C}$. In addition to temperature, RH is indicated to affect the primary particles size as well. By assuming a geometric

standard deviation (σ_g) of 2.0, and assuming a lognormal size distribution, the consistency of these values and those coming from earlier studies for sodium-based aerosols can be noted. Nevertheless, some authors (Sundarajan et al., 1982) found that the initial sodium fire aerosol distribution was bimodal.

In-containment aerosol phenomena

A thorough aerosol phenomenological description requires knowledge of some fundamental properties like size, shape, density and chemical composition, as well as particle dynamics. The former are dependent on particle-particle (agglomeration) and particle-gas/vapour interactions (vaporization/condensation); the latter is a result of the net effect of various driving forces that are usually estimated in terms of process rates.

A set of studies found in the open literature allows identification of potential prevailing conditions in containment in the case of a CDA. Using CONTAIN-LMR/1b-MOD1 (Murata et al., 1993) and assuming a breach of the primary coolant boundary in the Advance Liquid Metal Reactor (ALMR), Chiao et al. (1994) demonstrated that consequences of pool and spray fires could be drastically different in terms of the thermal characterization of the containment atmosphere depending on specific conditions such as the amount of steam in the atmosphere and the sodium inventory reaching the containment (sprays). Fig. 8 displays the containment response in the case of a pool fire. Pool fires lead to pressure increases of about 0.6 atm ($P_{\text{peak}}=1.7$ atm) and maximum containment-atmosphere temperatures around 315°C; these spikes decrease over time and, in the long run (over 400 min), the temperature approaches values around 150°C and the pressure spike practically disappears. These numbers contrast with those from the spray scenarios where pressure rise can be as much as six times higher ($P_{\text{peak}}=4.3$ atm) and atmosphere temperature can reach 1067°C (assuming that 136 kg of Na entered the containment in 1 s).

Fig. 8. ALMR containment response to a sodium pool fire.

These analyses agree with previous ones that also pointed to a spray fire posing more challenges to containment integrity than a pool fire (Bae et al., 1994; Malet et al., 1982; Morewitz, 1979). Fig. 9 and Fig. 10 show some of the results obtained in the Bae et al. (1994) studies, where the effect of the initial sodium temperature and the initial oxygen concentration were parametrically investigated. The main observations were that pressure and temperature increases were higher and faster in the case of spray fires, even if less Na was injected. It was observed that the maximum pressure rise was far below the theoretical maximum (estimated on thermodynamic grounds) and they only approach each other when Na is sprayed in ultra-fine drops (Morewitz, 1979).

Fig. 9. Thermohydraulic variables of pool fires: a) Temperature and b) Pressure.

Fig. 10. Thermohydraulic variables of spray fires: a) Temperature and b) Pressure.

Analyses of large-scale containment response to postulated CDA scenarios were carried out for the Clinch River Breeder Reactor Plant (CRBRP) (Heisler and Morewitz, 1979). They investigated the effect of the extension of Na combustion in the thermal-hydraulic response of the building by calculations with the SOMIX code. They found that the maximum pressure increase was in all the cases far from a threshold (6 atm) identified as the maximum practical pressure. In fact, in no case did they get pressure increases over 2.1 atm. Some interesting outcomes from their study were: maximum temperatures (1800°C) and pressures (2.1 atm) were reached both for 27% and 84% of the oxygen reacted; and, no less important, substantial temperature gradients could be created in the containment, the profiles being a function of the amount of O_2 reacted. Fig. 11 illustrates this last observation.

Fig. 11. Temperature axial profiles as a function of initial Na amount.

Aerosol evolution: available data, deposition mechanisms and interaction processes

A number of experimental programmes were carried out in the past to understand the in-containment evolution of aerosols in the hypothetical case of an accident in a SFR. Many of those test campaigns were linked to code development and/or validation. Below a synthesis of their major observations is proposed.

ORNL (Adams et al., 1980, 1979) conducted a set of tests within the NSPP (Nuclear Safety Pilot Plant) facility (38.3 m³). In addition to the study of aerosol behaviour in enclosures, they addressed specifically the potential interaction between two different aerosol populations. To do so, sodium oxide aerosols and uranium oxide aerosols were generated. Additionally, they reported on the different characteristics of Na₂O aerosols from pool and spray fires. As generic findings confirming some of the statements made in previous sections, they noted a much bigger impact on thermal-hydraulics from Na-spray oxidation than from that of a pool. This difference extends also to the airborne aerosol concentration, which reached levels between 40-60 g/m³ in the case of spray fires, whereas it was notably lower (6-25 g/m³) for pool fires (using the same amount of Na). They also reported on the Na₂O particle size from these two sources, but it is not clear if this comparison can be made since they used different diameters to characterize the distribution (no geometric standard deviation is even given). Anyway, it was seen that in all the individual aerosol tests the U₃O₈ concentration was notably lower (0.05-0.22 g/m³) and the associated particle sizes were smaller than that measured in the Na₂O tests.

The Na_2O pool-fire experiments showed a clear exponential decay in aerosol concentration. When comparing Na_2O and U_3O_8 depletion kinetics, it is noted that Na_2O underwent faster removal (Fig. 12). In addition to the depletion kinetics of the single-component aerosol tests, the dual-component aerosol tests showed that the aerosol species co-agglomerated and, as a consequence, affected each other.

Fig. 12. Aerosol concentration vs. time.

Fig. 13 shows how the depletion kinetics was increased when injecting the second source of aerosols. By estimating the depletion rates of single and dual-species tests in both figures, it is realized that adding a new aerosol in the vessel meant an increase of the depletion rate by a factor between 2 and 3. The final mass distribution of these multiple-source tests confirmed the two compounds' co-agglomeration.

Fig. 13. Concentration evolution: single vs. multiple species aerosols.

The above observations regarding differences between aerosols from pool and spray fires were also highlighted by Cherdron et al. (1985) in the FAUNA facility (220 m³). As shown in Fig. 14, where spray aerosols were generated in a very short period of time (around tens of seconds), the maximum aerosol concentration was much higher than that of pool-fire tests. Deriving the time for the maximum aerosol concentration to reduce by a factor of 100, it would take around 100 h for pool-fire aerosols and between 0.5 and 1 h for that of spray fires; in other words, in the conditions of the FAUNA tests, spray aerosols were removed nearly 100 times faster (but which attain, as stated above, substantially larger peak concentrations).

Fig. 14. Concentration evolution in the FAUNA facility.

Numerous studies (Adams et al., 1980, 1979; Jordan et al., 1988; Postma and Owen, 1980) have shown that in hypothetical accident conditions of SFRs, in-containment aerosols will undergo depletion processes that will carry a fraction of the airborne particles to containment floor and walls. Given the anticipated conditions in SFR containments, the major mechanisms expected to play a role would be: thermophoresis, which would take particles onto colder surfaces; gravitational settling, which would be effective for larger particles; turbulent deposition, which would be effective in those containment areas with highly turbulent flows (e.g., during Na-spray/Na-pool burning). Moreover, the efficiency of these removal mechanisms would be highly dependent on particle size, density and shape; all three of these features are governed by particle formation, agglomeration and vapour condensation (if any), especially water vapour given the hygroscopicity of the aerosols. Agglomeration occurs by different mechanisms, i.e., turbulence, gravity, Brownian diffusion, etc.

From all the above processes, in-containment thermophoresis is quite distinctive for Na aerosols. Specific studies were carried out to understand the effect of thermophoresis on Na₂O particles in a 2-meter-high chamber (Nishio et al., 1977). In particular, Nishio et al. looked at the combined effect of thermophoresis and “soaring” of aerosols by thermal convection which they considered to hamper settling. They concluded that thermal convection had a noticeably impact on both thermophoresis and sedimentation; thermophoretic velocity could be reduced by half, whereas the “soaring” effect was highlighted as an essential phenomenon in the early stages of a postulated SFR accident.

One uncertain variable affecting thermophoretic removal is the thermal boundary layer thickness (δ_T). It has been attributed different values (NEA-CSNI, 1979, Chapter III), but usually these ranged between 100 and 1000 μm .

Experiments conducted in large-scale facilities (Jordan et al., 1988; Postma and Owen, 1980) demonstrated that suspended aerosols were preferentially removed by settling, although plated mass (turbulence, diffusion and thermophoresis) was in no case negligible: in the FAUNA facility (220 m³) around 60% deposited onto the floor; in the ESMERALDA facility (3600 m³) only 10% of the mass deposited onto the walls (Jordan et al., 1988).

Agglomeration plays a key role in aerosol growth, particularly just above a pool fire. In the flame zone a high particle number concentration of small particles exists and, as a consequence, particle Brownian motion can result in substantial agglomeration rates. Above that region, the resulting larger particles are carried by thermal convection away from the burning zone and other agglomeration mechanisms (i.e., turbulent, gravitational,

inertial ...) may dominate. From that location upward it is expected that agglomeration becomes less relevant (NEA-CSNI, 1979, Chapter III); nevertheless, while its intensity may decrease, the high aerosol concentrations mean that agglomeration continues and it is a key factor in accelerating deposition by sedimentation.

The effect of agglomeration on aerosol depletion was studied experimentally by Nishio et al. (1977). Through a battery of experiments, he observed how airborne aerosol concentrations decayed following different rates depending on initial particle concentration. At low initial concentration a net exponential decrease is observed whereas at high concentrations (5000 mg/m^3) agglomeration accelerates the aerosol depletion at early times. As these experiments were part of a more ambitious programme mainly focused on thermophoresis, another variable investigated (not relevant for this discussion, though) was the facility heating. Some of their results are given in Fig. 15.

Fig. 15. Concentration decrease of sodium oxide aerosol (2000 W/m^2 heating).

Sodium vapour condensation onto sodium-compound aerosols (heterogeneous nucleation) plays also an important role in the region just above the vaporizing pool. The combined effect of condensational growth and stirred settling governs the aerosol behaviour in the space above a hot sodium pool. After the formation of oxide-aerosol fog, most of the aerosol is seen to be removed at an increasing rate until the cloud suddenly disappears (van de Vate et al., 1976); this was presumably for a more-or-less open

atmosphere. The aerosol settled on the sodium pool will, if sufficient, hinder the reaction of the pool surface with the atmosphere.

Adsorption of vapours onto aerosol particle surfaces, though less important to aerosol growth, is very important in determining the eventual attenuation in the containment of fission products in the vapour phase (as indicated in Section 2.1). Information is contradictory: experiments have generally shown that sodium oxides are very active in adsorbing fission product vapours (NEA-CSNI, 1979, Chapter III) while there is evidence that oxide on a pool surface has little retaining effect on fission products in the Na beyond mass-transfer effects (i.e., hindering evaporation from the liquid surface).

Equations describing aerosol mechanisms are developed based on fully-dense spherical particles. However, reality may be far from such an ideal situation; in other words, particles might be fluffy and irregular. In order to overcome the resulting shortcomings from the “ideal approximation”, equations are corrected by shape factors and/or effective densities. Two shape factors are usually considered: the dynamics shape factor (χ) and the agglomeration shape factor (γ) where the nearer the values of these factors are to unity the nearer the particle is to sphericity. The dynamic shape factor accounts for the effect of non-spherical forms on the drag force that a moving particle experiences. The coagulation shape factor corrects the actual target size that a particle exhibits when interacting with other particle. For sodium oxide aerosols formed in humid air containing CO₂, shape factors for agglomerates were measured to be about 1.3 (NEA-CSNI, 1979, Chapter III). Smaller values very close to unity were found for sodium peroxide aerosols in experiments by Barbe-Le Borgne et al. (1986). The presence of humidity has the effect of rendering particles more spherical where, in excess, it will convert oxide aerosols into droplets of hydroxide solution; we note, also, that sodium hydroxide is very hygroscopic and will convert to droplets at quite low relative humidity.

An alternate approach combining particle mobility and collision correction factors was proposed for sodium particles by Gieseke et al. (1977): sodium oxide agglomerates are assumed to be spherical but porous; in other words, they are characterized by a reduced effective density (ρ_a) and an agglomerate radius (R). Then particle dynamic equations are corrected through,

$$r_e = \alpha^{1/3} \cdot R \quad (2)$$

where α is the ratio of the actual and the theoretical densities and r_e is the particle equivalent radius.

Extensive experimental studies of sodium oxide agglomerates characteristics at BCL indicate a value for α of 0.18 for agglomerates containing about 200 primary particles formed in dry, CO₂-free air (Gieseke et al., 1977). Measurements of sodium oxide particles in moist air containing CO₂ indicated values for α averaging about 0.61 (NEA-CSNI, 1979, Chapter III).

1.3.3. Overall assessment of modelling capabilities

Given the practical absence of activity during the last 20 years in the field of CDA modelling beyond core-disruption aspects, the status of the mid-1980s computer codes may be considered applicable today to a good extent. The main insights into aerosol-modelling drawbacks at the time were reported by Dunbar et al. (1984) - see also Dunbar (1985) and Fermandjian (1985). In the late 1980s a benchmark against experimental data in a medium-scale facility (400 m³) for a 90-minute pool fire was conducted using a number of these aerosol codes - see Lhiaubet et al., 1990. While most of the codes then reviewed and tested are no longer available, much (if not all) of the aerosol modelling was subsumed in codes such as ASTEC (Van Dorsselaere et al., 2009), MELCOR (Gauntt et al., 2005) and CONTAIN (Murata et al., 1993) and conclusions from earlier work can be considered relevant to these codes. It is interesting to note that the Lhiaubet et al. benchmark concluded that aerosol codes were adequate for pool-fire conditions in the sense that they tended to be conservative by overestimating (but not massively) the suspended-aerosol concentration. This overestimation was in part due to significant underestimation of deposits on walls; this may mean that thermophoresis was underestimated or that account must be taken of mechanisms additional to those usually expected in the containment, e.g., turbulent deposition.

- **Agglomeration.** Several aspects of agglomeration were considered not to be properly taken into account in the models: particle shape, collision efficiency and turbulence (Dunbar et al., 1984).

Concerning shape, aerosol equations are developed for spherical particles but allow deviations from this by introducing two coefficients (shape factors); these intend to approximate (usually empirically) the effect of particle shape on their motion (dynamic shape factor, χ) and on their agglomeration rate (agglomeration shape factor, γ). However,

computer codes assumed no variation of χ with particle size and, occasionally, γ was adopted as a correction factor of the spherical particle surface instead of its diameter.

Gravitational collision efficiency had been approximated by either Fuchs or Pruppacher and Klett equations (Dunbar et al., 1984), the former being 3 times greater than the latter. The difference arises from the Fuchs model not taking account of the motion of the smaller particle with which the larger particle collides. Presently, the Pruppacher and Klett formulation for the efficiency factor has been adopted in the majority of nuclear safety computer codes:

$$\varepsilon(r_1, r_2) = \frac{1}{2} \left(\frac{r_2}{r_1 + r_2} \right)^2 \quad (3)$$

The effect of turbulent agglomeration was and is approximated by the Saffman and Turner equations (Saffman and Turner, 1956), which accounts for both shear effects and in-eddy acceleration. These equations rely also on parameters like collision efficiencies, shape factors and turbulent energy dissipation rate. In some present codes, e.g., CONTAIN (Murata et al., 1997), the shear collision efficiency is set to 1.0 whereas that of inertia is estimated through Pruppacher and Klett's model. Even though some settings have been adopted and become "standardized", these parameters are still largely uncertain.

- **Numerics.** At the time the models were reviewed, different numerical methods were being used in aerosol codes: the moments method and different versions of the sectional method (i.e., piecewise constant and piecewise linear). The former was observed to have severe drawbacks when dealing with high agglomeration systems and it was abandoned. As a result, most of present aerosol codes rely on discretizing the size domain to turn the integro-differential aerosol equation into a set of algebraic ordinary differential equations.

According to Dunbar et al. (1984), agglomeration issues should be investigated through analytical experiments. Likewise, integral experiments were recognized to be needed to assess the effect of aerosol injection (rates and total amount) from pool/spray Na fires on aerosol evolution within containment. This was investigated in the ABCOVE

programme (Aerosol Behavior COde Validation and Evaluation) carried out in the Containment System Test Facility (CSTF) at HEDL (Hilliard et al., 1985). Although a number of experiments were conducted in the CSTF facility, only three of them belonged to the ABCOVE programme. Nonetheless, these explored different aspects of aerosol generation: pool/spray sources, co-agglomeration, atmosphere composition, etc. A set of codes (i.e., HAA-3, HAARM-3, MAEROS, etc.) were compared to data and they all showed reasonable behaviour estimating airborne aerosol concentration and the total leaked mass was predicted within a 1.3 – 2.0 range from measurements, depending on the Na species (1.3 for NaI and 2.0 for NaO_x). However, it should be underlined that the consistency of calculated results with data required a set of parametric calculations to determine a correction factor ($\alpha \epsilon$) of particle density and collision efficiency; and, even doing so, the codes were noted to behave better once the aerosol injection period was over.

According to the above discussion and the principal developments in the nuclear aerosol field (see the major review by Allelein et al. (2009), it seems very probable that some of the main model limitations identified in the mid-1980s persist. This means that to achieve reliable computer-code studies that do not need preliminary parametric calculations (i.e., tuning), improvements to characterizing particles and particle-particle interaction processes are required. Concerning particle characterization, the major variables governing a more accurate description are density and shape; improvement would mean coming up with models and/or applicable correlations for effective density and dynamic and coagulation shape factors. Regarding particle-particle interaction processes, validation of available collision efficiency expressions under anticipated conditions within SFR containments as well as determination of those parameters involved in some agglomeration mechanisms, such as the turbulent dissipation rate, would be needed. In other words, aerosol transport mechanisms are accurate enough as long as particles and particle-particle interactions are well described.

Aerosol generation in SFR containments strongly depends on three major phenomena: sodium vaporization, chemical reactions with the surrounding gas, nucleation and primary particle agglomeration. Their consideration would require coupling thermal hydraulics, chemical reactivity of airborne and dissolved species, aerosol particle transfer and radiative heat transfer from sodium pool and spray fires (Yamaguchi, 2009). A demonstration of this was the CONTAIN-LMR/1B-Mod.1 code (Murata et al., 1993) which included models for sodium pool and spray fires by adapting models coming from the SOFIRE II (Beiriger et al., 1973) and the NACOM (Tsai et al., 1980) codes, respectively. The result of integrating these phenomena should be the prediction of proper particle composition, concentration and size. Given the mixing conditions of the atmospheric layer where chemical reactions and nucleation are occurring, as well as the

potential high concentration of the resulting primary particles, it is of utmost importance to achieve a good description of the appropriate agglomeration mechanisms in this region.

Another missing area in codes is fission-product partitioning. This is of utmost interest for source term predictions and, although some data are available, both equilibrium and kinetic studies should confirm and extend the available information. A separate study has also identified the high uncertainty associated with iodine chemistry in a SFR containment, Powers et al. (2010). Kissane et al. (2013) concluded that fission-product partition at equilibrium with liquid sodium would be the following (Table 8):

Table 8. Fission-product partition at equilibrium.

Element	Characteristics in Na(l)	State	Main location(s)
Noble gases Xe, Kr	Inert, almost-zero solubility	element	gas phase
Halogens I, Br	Very volatile but react with Na → low volatility	NaI, NaBr	mainly Na (l) some phase gas
Alkali metals Cs, Rb	Soluble, high volatility	Cs, Rb	some Na(l) mainly gas phase
Alkali-earth metals Sr, Ba	Low volatility either as metals or oxides	SrO, BaO in suspension; Sr, Ba soluble in Na(l)	Na(l)
Noble metals Ru, Pd, Rh, Ag	Very-low solubility (except Ag), very-low volatility	metallic, in suspension	Na(l)
Other metals Mo, Tc	Very-low volatility	metallique &/or oxide, in suspension	Na(l)
Actinides, U, Pu	Very-low volatility	MetalO ₂ in suspension	Na(l)
Others Te	React with Na creating telluride of low volatility	Na ₂ Te, solid in suspension	Na(l)

In turn, this points to the need of having a chemistry and nucleation model for those fission products capable of significant escape from Na solutions, such as caesium. Present LWR codes do different things: e.g., some such as MELCOR assume that particles

nucleate as soon as vapour become saturated and allow no supersaturation; others such as ASTEC allow supersaturation and model kinetically the process of formation of aerosols by nucleation.

Therefore, current LWR integral codes would be capable of capturing in-containment source term evolution if they are improved with SFR aerosol generation and fission-product chemistry and partitioning models: this is a sine-qua-non condition to obtaining a credible characterization of particles and airborne fission-product inventory. Nevertheless, even if current LWR codes appear enabled with the major anticipated aerosol deposition mechanisms in SFR containments, it seems advisable to undertake a thorough-as-feasible validation campaign. For that purpose a sound and comprehensive database against which to compare code estimates would be instrumental; this database should take into account previous and valuable experimental campaigns such as the ABCOVE and FAUNA programmes.

1.4. Frame of the thesis

As a summary of the above section, it has been found that improvements to characterizing particles (i.e., density and shape) and particle-particle interaction processes are required. However, beyond any doubt, two of the strongest modelling needs for SFR accidents are: aerosol generation which, in turn, means to properly model sodium vaporization, chemical reactions with the surrounding gas, nucleation of combustion products and primary particle agglomeration; and fission product partitioning.

Given the practical absence of activity during the last 20 years in the field of CDA modelling beyond core-disruption aspects, the status of the mid-1980s computer codes may be considered applicable today to a good extent.

In the late 1980s a benchmark against experimental data in a medium-scale facility (400 m³) for a 90-minute pool fire was conducted using a number of these aerosol codes – see Lhiaubet et al. (1990). While most of the codes then reviewed and tested are no longer available, much (if not all) of the aerosol modelling was taken over in codes such as ASTEC (Dorsselaere et al., 2009), MELCOR (Gauntt et al., 2005) and CONTAIN (Murata et al., 1993) and conclusions from earlier work can be considered relevant to these codes. The Lhiaubet et al. benchmark concluded that aerosol codes were adequate for pool fire conditions in the sense that they tended to be conservative by overestimating (but not massively) the suspended aerosol concentration. Later, Souto et al. (1994) demonstrated that the aerosol transport mechanisms were accurate enough as long as particles and

particle-particle interactions were well described by modelling the CSTF experiments with the MELCOR 1.8.2 code.

The current capability of LWR codes to model aerosol deposition within a SFR containment under BDBA conditions was tested by CIEMAT (Herranz et al., 2013). Through a systematic application of the ASTEC (Dorsselaere et al., 2009), ECART (Parozzi et al., 2012) and MELCOR (Gauntt et al., 2005) codes to relevant ABCOVE tests; insights were gained into drawbacks and capabilities of these computation tools. To accommodate differences in boundary conditions between LWR and SFR containments under BDBA, some hypotheses and approximations were adopted. Two major outcomes result from this study: a reasonable approximation to the BDBA scenario can be achieved with LWR codes if suitable hypothesis are made and development and implementation of new models is mandatory to enhance predictability to the required level in safety analyses. Vaporization, nucleation and oxidation of Na and turbulent agglomeration of particles are phenomena for which models should be developed and implemented. Furthermore, the importance of a good morphological characterization of aerosol particles has been highlighted.

In the light of this work, current LWR integral accident codes look promising as a computational platform to be extended to the SFR domain. They would be capable of capturing in-containment source term evolution if they are improved with SFR aerosol generation and fission product chemistry and partitioning models. Once they are adapted to anticipated SFR scenarios, extensive validation should be undertaken against a comprehensive and sound database.

In this context, among the European Collaborative Projects created under the 7th Framework Programme of the European Commission to study the main challenges of the Gen. IV technologies, the JASMIN (Join Advanced Severe accidents Modelling and Integration for Na-cooled fast neutron reactors, contract number 295803) project was born in order to extend to SFR the use of the ASTEC European code system, a computer modelling package for severe accidents in water-cooled nuclear reactors. The code objectives will be to predict throughout the primary phase of the accidental sequence the cladding and fuel behaviour as well as the behaviour of the released fission products both in the primary circuit and in the containment vessel, including the extreme thermal-hydraulic conditions prevailing in the case of sodium fire. Regarding in-containment source term predictability, the new ASTEC-Na code will integrate and capitalize on state-of-the-art knowledge of SFR accidents through the improvement of existing physical models or the development of new ones based on the needs of model development pointed out in the 7th Framework CP-ESFR project: particle generation and aerosol chemical transformations. This project subscribes to the general objective of enhancing the

resistance of Gen. IV SFRs to severe accidents, a major objective of the Strategic Agenda and Deployment Strategy set by the SNETP (Sustainable Nuclear Energy Technology Platform, <http://www.snetp.eu/>).

In the frame of the JASMIN project, a particle generation model to calculate the particle generation rate and their primary size during an in-containment sodium pool fire has been developed and implemented in ASTEC-Na code. This thesis is the result of this work.

Chapter 2

THESIS SETTING OUT

This thesis is a contribution to the technical understanding of the in-containment source term during postulated severe accident scenarios in sodium-cooled fast reactors.

2.1. Motivation

In SFR safety studies the highly-unlikely event of a core disruptive accident must be considered where this could lead to contaminated-sodium at high temperature leaking into the containment. In these conditions, the vaporization of sodium and its subsequent combustion with the oxygen available would result in the generation of supersaturated sodium-oxide vapours likely to nucleate and form particles. The aerosol formed and its chemical transformations would be responsible to a great extent for the radiological and chemical impact of any potential source term. Therefore, aerosol formation and subsequent behaviour in the anticipated accidental conditions are key phenomena to model to describe source term transport.

The computer codes used to analyse BDBA scenarios in SFRs have mostly focused on energetics and thermal-hydraulics (Murata et al., 1993) so that particle generation modelling has received much less attention. Several sodium fire studies (pool and spray fires) have been carried out since the 1970s, in facilities like PLUTON (Lhiaubet et al.,

1990) and JUPITER (Malet et al., 1990) in France, CSTF in the USA (Hilliard et al., 1979, 1977; McCormack et al., 1978; Souto et al., 1994), FAUNA in Germany (Cherdron et al., 1990, 1985; Cherdron and Jordan, 1983, 1980) or ATF in India (Baskaran et al., 2011; Subramanian et al., 2009; Subramanian and Baskaran, 2007). In all of them, the aim was to understand the sodium burning process and to study the sodium compound aerosols behaviour and their chemical composition. Since then a number of studies have intended to model the whole scenario with relative success.

The pioneering work by Beiriger et al. (1973), who developed a tool mainly focused on fire energetics (the SOFIRE code), was followed by others who made specific hypotheses and approximations. In the SOFIRE model, the formation of a thin vapour layer over the surface of the pool is not considered and the Na-O₂ reactions take place on the pool surface. Through an extensive review of the physico-chemical processes involved in the liquid sodium pool combustion, Newman (1983) established that pool combustion could occur via surface or gas-phase reaction depending on the ignition temperature. Based on this work, Sagae and Suzuoki (1985) developed an analytical combustion model in which sodium vapour diffuses from the pool surface to a flat flame where the Na-O₂ reactions take place. In this model the combustion rate depends on heat and mass transfer of Na and O₂ to the flame (flame sheet approach). The vapour-phase sodium-combustion model has been included in numerous combustion codes as the SPM code by Miyake et al. (1991), SOPA code developed by Lee and Choi (1997) or more recently in multi-dimensional numerical analysis codes such as the SPHINCS code (Yamaguchi and Tajima, 2003) or AQUA-SF code (Takata et al., 2003).

However, as said above, all these computer codes have mostly focused on energetics and thermal-hydraulics (Murata et al., 1993) so that particle modelling has received much less attention. For example: the SOFIRE code (Beiriger et al., 1973) assumes that all sodium-oxides produced becomes particles of a given size with no consideration of particle formation kinetics or primary-particle size; the CONTAIN-LMR code (Murata et al., 1993) requires the user to fix the initial particle size in the analysis and this becomes the size at which any particle is nucleated.

2.2. Objectives

The final objective of this investigation is to enhance the present model predictability of the in-containment source term in SFRs by bringing the gap from primary particle formation to final particle behaviour.

For that, a particle generation model has been developed as a step forward in the modelling of in-containment source term in SFRs. Besides, several specific objectives have been drawn:

- To better estimate the in-containment thermal-hydraulics boundary conditions during sodium combustion (3D simulations).
- To properly articulate all the phenomena involved in particle generation.
- Given the absence of experimental data on particle generation from sodium fires, to build up a theoretical database covering the foreseen range of potential scenarios.
- To validate the developed particle generation model.
- To derive correlations easily implementable in nuclear safety codes.
- Once generated a new code version including the derived correlations, to assess its performance against available large-scale separate effect tests.

2.3. Scope

This work presents the main features and bases of a particle generation model from sodium pool fires whose main output variables are particle generation rate and size and its performance assessment, once implemented in an integral severe accident tool (ASTEC-Na), against available large-scale separate effect tests.

The scope of the presented model is the estimation of particle generation by homogeneous and heterogeneous nucleation during an in-containment sodium pool fire in the near field of the pool. The main output of the model is the generation rate and size of the primary particles resulting from the sodium pool combustion. Therefore, any further consideration of particles growth by agglomeration, chemical reaction with steam and/or gases (like CO₂) and transport to other regions in the far-field of the pool, are out of the scope of the present investigation. Any of these additional phenomena would be essential for a full prediction of in-containment source term behaviour and, as such, they would be encapsulated in specific models in a lumped parameter code addressing SFR severe accidents, in which the present work would be embedded as a particle source into the containment atmosphere.

2.3.1. Thesis approach

The research approach has been stated through the performance of the three stages shown in Fig. 16:

- Compilation and understanding
- Development
- Model assessment

Through an exhaustive literature survey, two tasks have been addressed during the compilation and understanding stage. First, an experimental database on homogeneous nucleation has been developed covering the main techniques and materials usually employed in the experiments (see Appendix B). Secondly, a modelling approach has been carried out through the revision and study of the main theories on homogeneous nucleation. Simultaneously, a revision of the main characteristics of the ASTEC code has been done for a proper final model proposal.

The second stage, the developmental one, starts with the model assessment: the main approximations and hypothesis of the model has been done. Besides, an scenario analysis has been carried out and a theoretical database has been build up.

With the model assessment and the scenario analysis done and taken into account the main characteristics of the ASTEC code, a proposal of the model is done.

Fig. 16. Scheme of the research approach.

Therefore, from the research approach, the following specific tasks can be drawn:

- To review and investigate the fundamentals of homogeneous and heterogeneous nucleation models.
- Characterization of the in-containment thermal-hydraulics boundary conditions during sodium combustion through a Computational Fluid Dynamic (CFD) simulation. The simulation will be validated against experimental data.
- Assessment of the potential applicability of the current nucleation models under the studied conditions.
- Enhancement of the source term predictability through the development of a global particle generation model including all the phenomena from the sodium vaporization to the particle generation.
- Model implementation in a LWR code (ASTEC-Na code).
- Validation and/or verification of the implemented model.
- To come up with derived correlations to fill the gap of predictability.

This thesis is structured in 6 chapters. Chapter 1 introduces the Sodium-cooled Fast Reactors (SFRs): an overview is given with a short history of SFR development and their current framework. The bases of the SFRs technology are explained. Then, the importance of the Beyond Design Basis Accident (BDBA) scenario is shown. To finalize the chapter, the background and frame of the work is presented.

Chapter 2 is devoted to explain the investigation setting out: its motivation, objectives and scope. The thesis approach is also given in this chapter.

Chapter 3 is devoted to the development of the model. The conceptual scenario of a sodium pool fire is exhaustively analysed. Then, the four main branches of the Particle Generation (PG) model are explained and the main PG model results exposed.

In Chapter 4, the bases of the development of a zero-dimensional model are explained: the followed methodology, the adaptation process and the derived correlations for the PG model outputs, i.e., generation rate and primary particle size.

Chapter 5 is devoted to the assessment of the PG model. The implementation in ASTEC-Na code is explained in this chapter, and the main results from the assessment of the PG model are given.

To finalize, in Chapter 6 the main conclusions and final remarks of the present investigation are shown. Future work is proposed in this chapter.

Chapters 7, 8 and 9 are devoted to the published work in international/national papers and conferences, nomenclature and references, respectively.

Chapter 3

PARTICLE GENERATION MODEL

3.1. Conceptual scenario

Liquid sodium-pool combustion can proceed via surface reaction or gas-phase reaction depending on the initial pool temperature. Newman (1983) showed that when the pool temperature is lower than the ignition one (623-723 K), surface reaction dominates (oxygen diffusion into the pool), forming a grey-purple product close to the sodium surface that acts as a floating layer on the surface of the liquid sodium without any combustion; however, for sodium pool temperatures higher than the ignition one, this grey layer wets or decomposes allowing Na vapour to vaporize. Na vapour molecules diffuses away from the liquid surface and at a usually short distance from it, chemical reaction with O_2 in the air starts and combustion takes place. This region is called “flame region. Combustion in the flame region is dominated by O_2 diffusion into the pool. It is in this region where the sodium oxide vapours would form, nucleate and particle growth by vapours condensation onto primary particles takes place.

The gas-phase reaction region is sketched in Fig. 17, in which the Na pool is displayed as a hot flat plate. As observed, the pool nearby can be split into three layers: sodium vapour, right over the pool; a flame region, above and adjacent to the Na layer; and the bulk gas overlying the flame and feeding the flame region with oxygen by natural convection (Miyake et al., 1991; Newman, 1983; Newman and Payne, 1978).

At steady-state burning, the pool does not reach its boiling point but remains close to the commonly found equilibrium pool temperature of 1000-1010 K (Newman and Payne, 1978). On the other side, vapour pressure of sodium is approximately 1 kPa at 800 K and almost 20 kPa at 1000 K. In these conditions, sodium readily evaporates and this vapour will be transported by diffusion to the flame region in which Na vapour reacts with the available oxygen forming Na-oxides and making the local temperature rise to 1200-1300 K. Namely, sodium oxidation is sustained by Na diffusion and by O₂ brought to the region by turbulent convective flows in the gas over the pool surface. As sodium vapour supply by evaporation becomes relatively large and chemical reactions are known to be fast, sodium combustion will be governed by Na vapour supply by evaporation and oxygen transport into the reaction region. In the sodium vapour layer, a vertical laminar flux will exist from the sodium pool surface to the flame region, whereas in the flame region, the flow field will become fully turbulent under the natural convection regime for pool diameters larger than 0.1 m (Newman, 1983).

The Na-oxide compounds formed (Na₂O and Na₂O₂) have at the flame temperature vapour pressures well in excess of their saturation pressures, so that molecules cluster by homogeneous nucleation forming very small primary particles. As soon as these first seeds appear, several potential mechanisms are likely to occur as the presence of Na gas phase deposits on the existing aerosols and its subsequent oxidation of the vapour-phase oxide molecules on the surface of these nucleated particles if vapour pressure is higher than saturation pressure at the particle surface temperature (i.e., heterogeneous nucleation occurs).

Fig. 17. “Hot flat plate approach”.

3.2. PG model

Based on the conceptual physico-chemical scenario described above, global modelling of Particle Generation (PG model) has been developed. As a result, particle generation rate and primary-particle size can be obtained for a sodium pool fire in a SFR containment. In this model, steady-state burning is assumed.

The PG model comprises the individual phenomena involved in the particle generation process during a sodium pool fire, namely: Na vaporization, O_2 natural convection, Na- O_2 chemical reactions and vapour-to-particle conversion of Na oxides. The PG model sequence diagram is shown in Fig. 18. From the sodium pool definition by the pool temperature and the pool diameter, the vaporized Na from the pool surface is obtained through a Sodium Vaporization Model (SVM). Due to the extreme foreseen conditions above the combustion zone (high turbulence is foreseen), a steady 3D Computation Fluid Dynamics (CFD) approach is employed based on the FLUENT code (ANSYS Inc., 2008). In this numerical simulation, the O_2 natural convection and the Na- O_2 chemical reactions are modelled (O_2 Supply Model, O_2SM ; Na- O_2 Chemical Model, $Na-O_2ChM$) for an appropriate estimation of the thermal-hydraulic boundary conditions in

the region of interest, i.e., in the close vicinity of the sodium reaction zone. In the Vapour-to-Particle Conversion model (VtPCM), particle generation by homogeneous nucleation and particle growth by condensation are accounted for. As a result, the PG model produces the total number rate of generated particles (N) and the Primary Particle Size Distribution (PPSD) during an in-containment sodium pool fire.

Fig. 18. PG model diagram.

3.2.1. Sodium vaporization model

In order to couple the liquid-sodium pool to the gas phase equations in FLUENT, the sodium vapour flux emerging from the sodium pool surface is needed as an input for the FLUENT simulation.

Two approaches for the treatment of sodium pool combustion problem have been found in the literature. The first one, named as surface combustion model (Beiriger et al., 1973), is one in which Na vaporization rate is slow and Na-O₂ reactions occur at the pool

surface. The second one, a gas-phase reaction model, was developed by Sagae and Suzuoki (1985) and later used by Doda et al., 2003; Karthikeyan et al., 2009; Lee and Choi, 1997; Miyake et al., 1991; Yamaguchi and Tajima, 2009 and more recently by Sathiah and Roelofs (2014).

According to the Na temperatures around 800 K in normal operating conditions in the primary and secondary circuit (IAEA, 2006), a sodium vaporization model to simulate gas-phase combustion is proposed.

Sodium vapour pressure is low at pool temperatures of 800-1000 K; therefore, a diffusion flame is established very close to the sodium surface. In this boundary layer, the diffusion of heat and mass is dominant and the convection can be neglected. Based on a diffusion layer approach (gas-phase reaction model), an expression for the molar flux of sodium vapour is derived. In the boundary layer (between pool surface and flame), one-dimensional sodium vapour diffusion is assumed taking into account the diffusive resistance of N_2 to the sodium vapour movement toward the flame. As boundary conditions, sodium vapour pressure is assumed to be saturated at the pool surface and to fall down to zero concentration at the flame region edge facing the pool; the latter means that Na disappears instantaneously as soon as it interacts with oxygen (infinite chemical-reaction rate). It is also assumed that oxygen penetration into the evaporating-sodium boundary layer is negligible due to its consumption in the flame; this allows the sodium-vapour flux boundary layer to be treated as a sodium-nitrogen binary-diffusion problem:

$$\phi_{Na} = -\frac{D_{Na}}{l_f} \cdot X_{Na} \cdot C_{bl} \cdot \ln\left(\frac{X_{N_2,p}}{X_{N_2,f}}\right) = \frac{D_{Na}}{l_f} \cdot X_{Na} \cdot C_{bl} \cdot \ln\left(\frac{P}{P - p_{sat,Na}}\right) \quad (4)$$

where the logarithmic term describes the diffusive resistance that N_2 presents to Na vapour diffusion. In this equation, correlations for the physical properties of Na from Fink and Leibowitz (1995) are used. Besides, a correlation for the diffusion coefficient of Na through N_2 from the SPRAY code (Shire, 1977) is used:

$$D_{Na} = 0.9998 \cdot 10^{-9} \frac{T^{1.668}}{P} \quad (5)$$

The vaporized sodium molar flux-equation (Eqn. 4) involves two unknown variables, the distance between the flame and the pool surface (l_f) and the flame temperature (T_f). To determine these, the mass and energy conservation equations at the flame are solved. In this approach, a number of hypotheses are considered: flame surface area facing the pool is equal to the pool surface area (i.e., flame surface is assumed to be smooth and parallel to the surface); all the gases are considered ideal; and pool temperature is supposed to remain constant as a function of time, i.e., the heat transfer of the foreseen oxide layer formed on the pool surface to the un-burnt sodium is neglected.

Mass balance at the flame is given by the following equation:

$$\phi_{Na} = X \cdot \phi_{O_2} \quad (6)$$

where X is the oxygen-sodium stoichiometric ratio which is dictated by the chemical reactions described in section 3.2.3 (Karthikeyan et al., 2009). In this equation, infinite rate chemistry is supposed, i.e., all the O_2 coming to the flame is instantaneously consumed by the Na vapour.

The supply of oxygen from the environment to the flame is driven by natural convection. As the Lewis number ($Le = Sc/Pr$, and defined as the ratio of thermal diffusivity to mass diffusivity) for this mass transfer system of sodium vapour and air becomes almost unity, the molar oxygen flux is determined by using the heat/mass transfer analogy (Nu/Sh):

$$\phi_{O_2} = \frac{D_{O_2}}{L} \cdot X_{O_2} \cdot C_g \cdot Sh \quad (7)$$

where the McAdams correlations are used according to the scenario of interest (laminar/turbulent) (Incropera and Dewitt, 2011):

$$Nu = 0.54 \cdot Ra^{1/4} \left(10^4 \leq Ra \leq 10^7, Pr \geq 0.7 \right) \quad (8)$$

$$Nu = 0.15 \cdot Ra^{1/3} \left(10^7 \leq Ra \leq 10^{11}, all \text{ Pr} \right) \quad (9)$$

The general heat equation at the flame can be expressed as follows:

$$m \cdot c_p \cdot \frac{dT_f}{dt} = E_{chem} + H_{gf} - E_{fNa}^{cond} - E_{fg}^{conv} - E_f^{rad} \quad (10)$$

where T_f is the flame temperature, E_{chem} is the combustion energy generated at the flame, H_{gf} is the enthalpy transferred by material fluxes of different species (sodium, oxygen and sodium oxides) to the flame, E_{fNa}^{cond} is the conductive-convective energy transfer from the flame to the pool surface, dominated by conduction, E_{fg}^{conv} is the conductive-convective energy transfer from the flame to the environment, and E_f^{rad} is the energy transfer by radiation from the flame to the pool surface and from the flame to the atmosphere and walls surrounding the pool.

The energy transferred from the flame by radiation influences combustion rate. According to Yamaguchi et al. (2006) studies on flame emissivities in sodium pool fires, the emissivity is strongly dependent on the aerosol cloud around the flame and it will increase at the start of the fire. As the flame emissivity becomes larger, the global heat transfer from the flame to the pool surface (conduction plus radiation) decreases over time because of the flame temperature drops due to the extra heat loss by radiation (Sagae and Suzuoki, 1985); therefore, the evaporation from the sodium pool surface decreases. Flame emissivity values have not been found in the open literature. Through numerical experiments, Yamaguchi and Tajima (2003) estimated flame emissivity from 0.2 to 0.8 depending on the boundary conditions (pool and gas temperatures and O_2 concentrations). Therefore, due to the high uncertainties in the flame emissivity, an estimation of the radiation effect on the sodium vaporized flux has been developed assuming maximum flame emissivity of 0.8. Furthermore, the maximum radiative transfer is fostered by considering view factors of unity. With these conditions of maximum radiation, variations in the sodium flux less than 10 % have been found. Therefore, in steady-state conditions ($dT_f/dt=0$) and by assuming no radiation from the flame, the energy balance at the flame can be approximated as:

$$E_{chem} + H_{gf} = E_{fNa}^{cond} + E_{fg}^{conv} \quad (11)$$

3.2.2. Oxygen supply model

The oxygen supply to the flame region is the consequence of natural convection over the flame region: given the significance that O₂ supply might have in the entire scenario and due to the extreme foreseen conditions above the combustion zone where high turbulence can be anticipated, a computational fluid dynamic model has been developed with the FLUENT 14.5 code (ANSYS Inc., 2008).

FLUENT is a commercially available CFD tool whose formulation and numerics have extensively validated by a good number of research and industrial teams. Several methodologies are available for the resolution of the Navier-Stokes equations in FLUENT.

Direct solution of them (DNS) is not possible for the present problem due to the fine time and space resolution needed. Large-Eddy Simulations (LES) resolve only the large-scale turbulence and account for the smaller scales with subgrid-scale modelling. However, such simulations are still very onerous (of the order of weeks on an ordinary computer for rather simple flows). As the scenario under modelling is highly complex, finally, the Reynolds Averaged Navier-Stokes (RANS) methods fulfil the compromise between accuracy and computational costs (Andersson et al., 2012) by simplifying local turbulent fluctuations. With this model for steady-states, the equations of continuity, momentum and energy in Cartesian form can be written as follows:

$$\text{Continuity:} \quad \frac{\partial}{\partial x_j} \rho u_j = 0 \quad (12)$$

$$\text{Momentum:} \quad \frac{\partial}{\partial x_j} \rho u_i u_j = -\frac{\partial}{\partial x_j} P + \frac{\partial}{\partial x_j} (\tau_{ij} - \overline{\rho \mu_i \mu_j}) \quad (13)$$

$$\text{Energy:} \quad \frac{\partial}{\partial x_j} \left[\rho u_j \left(h_s + \frac{u_i u_j}{2} \right) + u_j P + q_j - u_i \tau_{ij} \right] = 0 \quad (14)$$

Turbulence effects have been simulated by adopting the SST k - ω model, as recommended by Menter (1994). In this model, the advantages of both k - ϵ and k - ω models are included (i.e., the robustness in the near wall-region of the k - ω model plus the accuracy of k - ϵ in the far field), which makes calculations computationally efficient in all regards.

The transport equations of the turbulent kinetic energy (k) and the specific dissipation rate (ω), together with the Boussinesq hypothesis to relate the Reynolds stresses to the mean velocity gradients close the system equations of continuity, momentum and energy are given by:

$$\frac{\partial}{\partial x_i}(\rho \cdot \phi \cdot u_i) = \frac{\partial}{\partial x_j} \left(\Gamma_\phi \cdot \frac{\partial \phi}{\partial x_j} \right) + G_\phi - Y_\phi (+D_\omega) \quad (15)$$

$$-\rho \cdot \overline{\mu_i \mu_j} = \mu_\tau \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \left(\rho \cdot k + \mu_\tau \frac{\partial u_i}{\partial x_i} \right) \cdot \delta_{ij} \quad (16)$$

where ϕ denotes the independent variable (k and/or ω) and G , Y and Γ represent generation, dissipation and effective diffusivity of the given quantity, respectively. The set of equations are solved using a segregated implicit solver with a second-order discretization scheme.

3.2.3. Sodium-oxygen chemical model

A number of sodium pool fires experiments are reported in the literature. Cherdron and Charpenel (1985) and Hilliard et al. (1979) performed large scale aerosol behaviour test in CSTF and FAUNA facilities, respectively. Malet et al. (1990, 1982) conducted sodium pool experiments to study the influence of sodium temperature, combustion area and atmosphere composition on the fire evolution. In all of them, the major species identified were oxide, Na_2O , and peroxide, Na_2O_2 .

A more detailed analysis of the chemistry of sodium pool combustion was developed by Newman (1983) in his review of sodium pool fire tests carried out during

the 1960s and 1970s. However, intermediate reactions and products were not clearly identified.

Based on the information found in the open literature on sodium pool fire analytical models (Karthikeyan et al., 2009; Lee and Choi, 1997; Marimuthu, 1996; Miyake et al., 1991; Sagae and Suzuoki, 1985), two reactions are considered in the Na-O₂ chemical modelling:

We note that some authors assert that reaction (17) is always the first oxidation step and, if there is sufficient oxygen, the sodium oxide produced is further oxidized to peroxide. In the present modelling and taking into account the very short time scale of interest for primary particle generation, formation of both oxide (Na₂O) and peroxide (Na₂O₂) are assumed to be infinitely fast, so that the relative proportion of each species in the products is governed by stoichiometry. That is, each 4 Na moles yield one mole of Na₂O and 1 mole of Na₂O₂; this means that in terms of mass fractions, of the total Na oxide species formed (Na_xO_y), around 40% is Na₂O and the remaining 60% is Na₂O₂.

During sodium pool combustion, the reaction of Na with the water vapour present in the atmosphere is also possible. However, as in most practical cases the oxygen is the major constituent, it is the oxidation of O₂ the dominating reaction (Yamaguchi et al., 2006; Yamaguchi and Tajima, 2003). As a consequence, this reaction is not here considered. For reacting flows, FLUENT provides several models for chemical species transport and chemical reactions. Among them, Generalized Finite-Rate Model is based on the solution of transport equations for species mass fractions, with the chemical reaction mechanism defined by the user. In this model, the conservation equations for chemical species are solved by predicting the local mass fraction of each species, Y_i , through the solution of a convection-diffusion equation for each species:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i \quad (19)$$

The mass diffusion in turbulent flows is calculated in this model by the following expression:

$$\vec{J}_i = - \left(\rho D_{i,m} + \frac{\mu_r}{Sc_t} \right) \nabla Y_i \quad (20)$$

The reaction rates that appear as source terms in the convection-diffusion equation (R_i) are computed by the eddy-dissipation model in which the reaction rates are assumed to be controlled by turbulence mixing and the Arrhenius chemical kinetic is not calculated. This model can be selected assuming Na-O₂ reactions are infinitely fast (Miyake et al., 1991). The net rate of production of species i due to reaction r , $R_{i,r}$, is given by the smaller of the two expressions below:

$$R_{i,r} = v'_{i,r} M_{w,i} A \rho \frac{\varepsilon_T}{k} \min \left(\frac{Y_R}{v'_{R,r} M_{w,R}} \right) \quad (21)$$

$$R_{i,r} = v'_{i,r} M_{w,i} A B \rho \frac{\varepsilon_T}{k} \frac{\sum_P Y_P}{\sum_j v''_{j,r} M_{w,j}} \quad (22)$$

The default values in the code for the empirical constants A and B have been used ($A=4.0$ and $B=0.5$).

3.2.4. Vapour-to-particle conversion model

As stated by Newman (1983), the combustion mechanism between sodium vapour and oxygen in the gas phase is followed by the formation of a condensed oxide by homogeneous and heterogeneous nucleation.

Once the supersaturated vapours have been formed in the gas phase after sodium oxidation, the system is in a non-equilibrium state. To reach equilibrium, the surplus of vapour molecules condenses (homogeneous nucleation) forming primary clusters on which other vapour molecules might condense (heterogeneous nucleation).

3.2.4.1. Homogeneous nucleation

Homogeneous vapour-liquid nucleation is a fundamental mechanism of phase transformation. The nucleation process involves formation of clusters in a metastable bulk vapour by thermal fluctuations: the passage from a metastable state over an energy barrier for the system to reach its thermodynamic equilibrium.

Even though nucleation has been studied since the 18th century, a reliable theoretical formulation has been difficult to derive. Major reviews of nucleation modelling exist (e.g., Ford, 2004; Kashchiev, 2000; Vehkamäki, 2006). Based on these, a diagram of evolution of nucleation theories is shown in Fig. 10. According to the scheme, Transition State Theory (TST) can be considered as the first theory of nucleation (Ford, 2004). Within the framework of the free-energy fluctuations theory, the probability of forming a critical cluster is exponentially related to the Gibbs free energy of cluster formation. The proportionality constant in the nucleation rate equation was included by Volmer and Weber (1926) by their kinetic interpretation of nucleation phenomena: nucleation is understood as a set of collisions, and the only important transitions are those that are brought about by the addition or loss of single molecules to form the cluster. The theory of Volmer and Weber was extended a few years later by Becker and Döring, 1935; Farkas, 1927; Zeldovich, 1942 and is now known as Classical Nucleation Theory (CNT). From the CNT, the evolution of analytical nucleation theories has been driven through two main branches (Fig. 19). On one side, adjustments of the CNT with “minor” corrections (phenomenological approaches); on the other, approaches developed for a more exhaustive description from the microscopic point of view. Among the microscopic theories, there are two main streamlines. On one side, the approaches based on defining a cluster by imposing geometric constraints on the molecular positions (Senger et al., 1999; Stillinger, 1963); on other side, the Density Functional Theory (DFT) (Oxtoby, 1998; Oxtoby and Evans, 1988) in which the key assumption in the phenomenological approaches – capillarity approximation – is removed and the free-energy barrier to nucleation is calculated in a non-classical manner using a mean field theory in which the molecules forming the cluster move in an effective potential field created by the other molecules in the cluster (Ford, 2004).

The simplest phenomenological adjustment is the Internally Consistent Classical Theory (ICCT) developed by Girshick et al. (1990) in which an unevaluated normalization constant in the nucleation rate expression is introduced. The Fisher droplet model (1967) is a slightly more sophisticated approach in which parameters are introduced in the work of formation to ensure that the model correctly reproduces known properties of clusters and vapours, including virial coefficients and critical properties. Dillmann and Meier (1989) developed a model based on the Fisher model using the observed critical-vapour properties and the second virial coefficient. The model is based on considering the curvature dependence of the droplets surface tension and additional degrees of freedom in the definition of the Gibbs free energy variation. However, the success of this model is challenged by correction of an inconsistency that leads to large changes in the predicted nucleation rate (Ford et al., 1992). Finally, Scaled Nucleation Theory (SNT), proposed by Hale (1986), is based on CNT but employing simplified models for the surface tension and liquid density based on scaled behaviour near the critical point.

Fig. 19. Overview of the main analytical theories on homogeneous nucleation.

Based on the review and analysis of the available models in the literature, it has been concluded that both the Classical Nucleation Theory (CNT) and the Internally Consistent Classical Theory (ICCT) might be suitable approaches for the assessment of the nucleation rates in the case of an in-containment sodium-pool fire. The reasons for that are:

- The higher complexity of later theories.
- The inherent uncertainty coming from the lack of information on Na_xO_y properties.
- The huge sensitivity of any homogeneous nucleation theory to variations in boundary conditions (i.e., temperature).

In addition, the complexity of other theories entails an extra numerical burden and the supposed gain in accuracy vanishes due to the intrinsic uncertainties in additional properties and estimation of key variables.

The CNT considers that the probability of attaining a cluster of a critical size (minimum number of particles to form a stable cluster) is exponentially related to the energy necessary to form it. The expression of the nucleation rate derived from the work of Becker-Döring, Frenkel, Farkas and Zeldovich is given as (a complete development of the model is done in Appendix A):

$$J_{CNT} = J_0 \cdot \exp\left[-\frac{\Delta G^*}{k_B T}\right] \quad (23)$$

where the energy barrier to form a cluster (ΔG^*) is the minimum of the classical Gibbs free energy for the formation of a droplet. The change of Gibbs free energy (ΔG) is the difference between a mechanical term proportional to the surface tension (associated with the creation of a spherical interface) and a thermal term proportional to the logarithm of the saturation ratio of the free vapour (coming from the difference in the Gibbs free energy of the liquid and vapour states, i.e., the phase change from supersaturated vapour to condensate) (Seinfeld and Pandis, 2006):

$$\Delta G = 4\pi \cdot r^2 \cdot \sigma - ik_B T \ln S \quad (24)$$

where i is the number of molecules forming the cluster and S is the saturation ratio ($S = p_{\text{vap}}/p_{\text{sat}}(T)$). This expression relies on the capillarity approximation that considers extremely small particles with the same surface tension as a liquid planar surface.

Therefore, the nucleation rate expression in CNT is as follows:

$$J_{\text{CNT}} = \left(\frac{2\sigma}{\pi m_l} \right)^{1/2} \cdot v_l \cdot N_l^2 \cdot \exp \left[-\frac{16\pi}{3} \cdot \frac{v_l^2 \sigma^3}{(k_B T)^3 (\ln S)^2} \right] \quad (25)$$

This expression can be explained as formed by two contributions. On one side, the pre-exponential factor involves specific features of the kinetics of the process as the collision probability of individual vapour molecules with critical clusters of the new phase. On the other side, the exponential factor reflects the thermodynamic aspects of the theory: the thermodynamically stable phase corresponds to the minimum Gibbs free energy of formation that represents the barrier for the transition of the system into the new phase.

The critical particle size is obtained by applying the extreme condition in the Gibbs free energy of formation ($[d\Delta G/dr]_{r^*} = 0$):

$$r^* = \frac{2\sigma v_l}{k_B T \ln S} \quad (26)$$

The simplest phenomenological adjustment to CNT is the Internally Consistent Classical Theory (ICCT) developed by Girshick et al. (1990). To overcome the limiting inconsistency in CNT, a kinetic normalization constant is introduced in the Boltzmann's distribution for the cluster population at equilibrium. This results in a new expression for the nucleation rate that is related to the CNT expression as follows:

$$J_{\text{ICCT}} = \frac{\exp \left(\frac{\sigma s_l}{k_B T} \right)}{S} \cdot J_{\text{CNT}} \quad (27)$$

The sensitivity of both theories to variations in boundary conditions (temperature) has been tested against experimental data. Given the absence of data on homogeneous nucleation in sodium oxides, experimental data on homogeneous nucleation in water has been used (Viisanen et al., 1993). Measurements of the rate of homogeneous nucleation were performed using an expansion chamber capable of producing short pulses of nucleation. The vapour-carrier-gas mixture is adiabatically expanded to a lower pressure and consequently to a lower temperature within a few milliseconds. The expanded, supersaturated state during which nucleation can occur is maintained for about 1 ms. Then a small recompression is performed to quench the nucleation process. Assuming the nucleation process to be stationary, the experimental nucleation rate will be given by the ratio between the number density of nuclei formed during the pulse and the duration of the pulse.

Fig. 20 shows the experimental homogeneous nucleation rate (J_{exptl}) as a function of supersaturation ratio (S) for water at different temperatures. From the figure follows the great sensitivity of homogeneous nucleation with temperature: slopes from 259 K to 217 K vary two orders of magnitude. This means that a simple theoretical model with a reasonable accuracy (CNT or ICCT) should be adequate to be implemented in a lumped parameter code in which boundary conditions are given by average values.

Fig. 20. Isothermal homogeneous nucleation versus saturation ratio.

In Fig. 21, the ratio of the theoretical-to-experimental nucleation rates as a function of the saturation ratio is presented for water. From the figure, CNT predicts nucleation rates within a couple of orders of magnitude in the case of water. ICCT predictions are between 4 and 6 orders of magnitude beyond the experimental data.

Fig. 21. Theoretical-to-experimental ratio of nucleation rates versus S .

In spite of the limitations in the CNT, CNT successfully predicts nucleation rates within a couple of orders of magnitude in the case of water and for a given range of temperatures (Ford, 2004). On the other side, the unevaluated normalization constant introduced in the ICCT to bridge some inconsistencies found in the CNT is an arbitrary modification and its successful in accounting data is mixed. In the light of the foregoing, it is concluded that CNT is an appropriate approach to model homogeneous nucleation in the conditions of interest.

3.2.4.2. Heterogeneous nucleation

The growth mechanism by heterogeneous nucleation (condensation on existing particles) has been extensively documented in the literature (e.g., Friedlander, 2000; Hinds, 1999; NEA, 2009, n.d.; Seinfeld and Pandis, 2006). The rate of aerosol growth by condensation will depend on the saturation ratio, particle size and particle size relative to the gas mean free path (Hinds, 1999). For particles much larger than the mean free path

(Knudsen number lower than unity, $Kn < 1.0$), the rate of condensation is controlled by the rate at which vapour can diffuse toward the particle surface. However, for particles much smaller than the mean free path ($Kn \gg 1.0$), the rate of particle growth by condensation will be governed by the rate of random molecular collisions between the particle and the vapour molecules. It is noted that Fuchs and Sutugin (1969) developed a formulation covering both the high and low-Knudsen number ranges including the transition regime.

As the critical particles generated by homogeneous nucleation are foreseen to be in the order of nanometres (NEA-CSNI, 1979), the prevailing conditions for heterogeneous nucleation fall in the free molecular regime (i.e., $Kn = 2\lambda/d_p \gg 1.0$). Therefore, the removal of vapours by condensation is calculated as the net flow of molecules attached to the surface of a particle of a given size by collisional impact (kinetic theory).

In the kinetic regime, the net flow of vapour molecules toward a particle is given by:

$$F = \frac{z \cdot a}{N_{AV}} \quad (28)$$

where z is the collision rate per unit area:

$$z = N_{AV} \cdot \bar{c} \cdot n \quad (29)$$

Therefore, in this formulation the condensation rate can be expressed as:

$$F = \frac{z \cdot a}{N_{AV}} \approx \frac{\pi d_p^2}{(2\pi m_1 k_B T)^{1/2}} (p_{vap} - p_{sat}) \quad (30)$$

In this expression, the Kelvin effect, i.e., the effect of surface curvature is neglected as a simplification (Friedlander, 2000). During condensation, particle latent heat is released at the particle surface. In these conditions, convection is an inefficient means of heat transfer since the particles are very small and move with little slip along with the gas; the same occurs with radiation since all the particles have roughly the same temperature. Otherwise, conduction through the gas phase is available for heat removal from the

particle surface where condensation is taking place, so condensation might be limited by the rate of heat removal from the particle surface. In our approach, however, the reduction of the condensation-rate due to the rise in the temperature from the release of latent heat has not been taken into account as no data on Na_xO_y diffusion coefficients are found in the available literature. These approximations (neglect of both curvature and latent heat) might lead to an over-estimation of the arrival of vapour molecules to the droplet surface, i.e., an over-estimation of the condensation.

By considering the rate of change of particle volume as:

$$\frac{dV}{dt} = F \cdot v_1 \quad (31)$$

The resulting particle size is given by the following growth law expression (Friedlander, 2000):

$$\frac{dd_p}{dt} = \frac{2v_1}{(2\pi m_1 k_B T)^{1/2}} (p_{vap} - p_{sat}) \quad (32)$$

In this approach, growing particles are assumed to remain in kinetic-regime conditions. During the initial stages of particle growth, this can be considered as an adequate approximation since condensation occurs on sub-micrometre particles coming from homogeneous nucleation (Shaw, 1989).

3.2.4.3. The single-burst approach

As shown in previous sections, vapour pressure is a key variable defining any particle formation in a supersaturated vapour. Homogeneous nucleation will reduce the number of free condensing molecules available and, hence, vapour pressure. But also, heterogeneous nucleation drivers will bring vapour molecules onto primary particle surfaces where they condense and further reduce vapour pressure. To calculate the particle generation rate an primary particle size by vapour-to-particle conversion in the analysed region, a program in FORTRAN 95 has been developed (see Appendix C).

Therefore, the total number of particles formed will be given by the nucleation and condensation as simultaneous and competitive processes (Clement and Ford, 1999a, 1999b; Warren and Seinfeld, 1985). Given that both processes are very fast, their full modelling (i.e., both phenomena competing for vapour molecules as a function of time) is an onerous computational burden since, for each time step, both nucleation and condensation should be calculated on a particle size distribution that would become more dispersed as time progresses. Instead, one may assume that after the first homogeneous nucleation, heterogeneous nucleation dominates from that time onward. In other words, this second approach neglects homogeneous nucleation beyond the first burst of primary particles. Both approximations are outlined in Fig. 22.

Fig. 22. Nucleation approaches.

Fig. 23 shows the number of generated particles by both approaches for a sodium pool fire of radius 5 cm (pool temperature of 1000 K and 21% of initial O_2 content). From the figure, the realistic approach (nucleation-condensation model) results are 3 times

larger than the single-burst approach. In the first one, it can be observed that from the first nucleation at 10^{-8} s, there is an abrupt increase in the generation of particles until $1.1 \cdot 10^{-7}$ s, reaching a value of $1.71 \cdot 10^{20}$ particles. At this point, there is no further particle formation due to the depletion of Na_xO_y vapour down to its saturation pressure by homogeneous nucleation and condensation, i.e., the nucleation process is cut-off. In the second one, however, homogeneous nucleation gives $5.13 \cdot 10^{19}$ particles at the start of the calculation. Both approaches agree with the idea of Clement and Ford (1999a, 1999b): particle production takes place in occasional and isolated bursts of nucleation and as foreseen, all the generated oxides produced during the sodium oxidation seem to be in particle form after a short period of time, of the order of 10^{-7} s. Concerning primary-particle size, both predictions give diameters in the nano-range, but with the diameters in the realistic approach approximately twice as larger as those in the single-burst approach.

As these estimates are strongly affected by uncertainties, a simple estimation of the error propagation linked to the properties used in the nucleation formulation has been developed to evaluate the minimum bands of uncertainties in the number of generated particles. Uncertainties associated to the theoretical expressions of homogeneous nucleation are not considered. Following the error propagation theory, the nucleation-rate expression uncertainties are calculated by the following expression:

$$\sigma_{J_{CNT}}^2 = \left(\frac{\delta J_{CNT}}{\delta \sigma} \right) \sigma_{\sigma}^2 + \left(\frac{\delta J_{CNT}}{\delta p_{sat}} \right) \sigma_{p_{sat}}^2 + \left(\frac{\delta J_{CNT}}{\delta \rho} \right) \sigma_{\rho}^2 \quad (33)$$

where the density and surface tension errors are evaluated based on the available information in the open literature (Janz, 1988). Regarding saturated-vapour pressure, the error has been evaluated based on the maximum difference found between the two available correlations (Jacq, 2006; Lamoreaux and Hildenbrand, 1984).

An upper uncertainty bound up to 2 orders of magnitude has been estimated. Therefore, by considering the estimated large uncertainties associated with the homogeneous nucleation model, we consider the single-burst approach to be accurate enough to describe the vapour-to-particle conversion process.

Fig. 23. Total number of generated particles by the two modelling approaches.

In this approach, the Na_2O and Na_2O_2 correlations of saturated-vapour pressure, density and surface tension as a function of temperature are needed to calculate the number of generated particles by homogeneous nucleation and its growth. As no information on Na_2O_2 density and surface tension is found, in this model both oxides are characterized by the same properties, i.e., both Na_2O and Na_2O_2 are treated as indistinguishable Na_xO_y as far as nucleation and condensation are concerned. Then, the correlations we use are the Na_2O saturated-vapour pressure proposed in Jacq (2006); regarding density and surface tension and in the absence of specific correlations for Na_2O , correlations for Na_2CO_3 are used (Janz, 1988).

3.3. PG model results

The available data in the literature to conduct a full and extensive validation of the model presented in previous sections, in terms of particle number and size, are scarce. Nonetheless, some measurements concerning the burning rate have been found and the model will be compared with these (next section). Then, the model performance will be assessed in a scenario whose conditions reflect those expected in the case of a realistic Na pool fire.

3.3.1. Partial validation

A partial validation of the PG model has been carried out based on the sodium pool experiments of Newman and Payne (1978). For benchmarking, estimates of burning rates based on the surface model included in SOFIRE code (Beiriger et al., 1973) have been added. SOFIRE is a reputable sodium pool combustion model based on the surface combustion approach (i.e., no Na vaporization is accounted for).

In Newman and Payne's experiments, the burning rates of sodium pool fires were measured for a sodium pool of 0.1 m diameter at sodium pool temperatures in the range of 523-1023 K and in natural-convection airflow conditions (oxygen molar fraction of 21%). Burning rates were measured by measuring the sodium pool mass change with time and by collecting the emitted smoke using a pumped filtering system.

The circumferential symmetry of the experimental scenario allows assuming circumferential symmetry (i.e., the same variables profiles are expected at any azimuth). The geometry and domain meshing of the problem is illustrated in Fig. 24. The sodium pool is represented by a surface of 0.05 m radius. The computational domain is rectangular, with 0.60 m height and 0.20 m length. The ratio of the pool surface area to the horizontal cross-sectional area of the domain is 0.065 which ensures that pool combustion is not influenced by the size of the domain; in other words, the vessel size does not influence the O_2 supply by natural convection over the horizontal combustion plane (Sagae and Suzuoki, 1985). For the non-uniform grid, 4001 quadrilateral cells are used to mesh the entire volume. The maximum nodes areas are outside the influence zone (10^{-2} m^2); however, inside the influence zone of the flame, a higher density mesh is used up to a minimum area of 10^{-6} m^2 . It is worth reminding that in this approach, the liquid sodium pool is modelled as a thermally thick solid, i.e., the sodium pool is assumed to be stagnant and the spreading of the sodium negligible.

Fig. 24. Meshing of the sodium fire simulation.

Fig. 25 compares the calculated burning rates of liquid sodium with the experimental results of Newman and Payne (1978). In addition, the Na burning rates calculated by the surface combustion model SOFIRE are included. Note that pool temperatures in the figure are over 800 K (i.e., in the gas-phase combustion regime).

From Fig. 25, the estimates-to-data agreement is outstanding. On the one hand, the experimental trend of increased burning rate with Na pool temperature is followed by the calculations. On the other hand, the data scattering helps predictions to be well within the measurements range. As can be observed, SOFIRE noticeably under-predicts the burning rates. Probably the major difference between both approaches concerns reaction temperatures: whereas in the gas-phase-combustion approach (PG model) the flame temperature is always higher than the pool one (1300 K and 1000 K according to Newman and Payne (1978)), the surface combustion approach takes the pool temperature as the

reaction temperature. This temperature discrepancy makes a difference in terms of reaction rates (Sagae and Suzuoki, 1985). In addition, oxygen transfer by natural convection to the flame will be fostered by the higher temperatures at the flame what, in turn, will lead to faster combustion.

These results seem to indicate that surface combustion is not conservative when applied at pool temperatures over 800 K since it would under-predict both the thermal load to the containment and the airborne-particle loading relative to what could be expected in the case of an in-containment pool fire.

Fig. 25. Burning rates vs. pool temperature.

3.3.2. PG model estimates

3.3.2.1. Main results

In order to show the PG model performance, a scenario thermally similar to the one foreseen in the case of a pool fire (i.e., atmospheric pressure and pool temperature of 1000 K) has been proposed in a geometry similar to the one used in Newman experiments (i.e., a 10 cm Na-pool diameter).

The velocity field is shown in Fig. 26. The general flow pattern is an ascending flow entering from the edge of the pool surface. The ascending flow velocity distribution

behaves like a plume: low horizontal velocities at the reaction zone (edge of the pool surface) and upward velocity increasing towards pool centre (maximum velocity of 1.185 m/s at 0.06 m above the pool surface at the centre) due to buoyancy forces mainly driven by temperature gradients. Inside the plume, velocities of 0.70 m/s are reached. Note that O_2 concentration drops in the air stream as oxygen is partially depleted while the flow moves towards the pool centre (Fig. 27).

Fig. 26. Flow velocities field (m/s).

Fig. 27. O₂ mass fraction field.

More linked to the particle generation are temperatures and Na-oxides partial pressures. The temperature field is shown in Fig. 28. Sodium burning starts at the edge of the pool surface due to fresh air entering into contact with sodium vapour by natural convection. The sodium-vapour combustion generates an ascending plume from the edge of the pool surface to the centre. A maximum temperature spot of 1448 K is produced where the oxidation starts while the temperature decreases along the plume to 1200-1300 K at 0.03 m from the pool centre. These estimates reasonably agree with the measurements made by Newman and Payne (1978) of 1300 K at the flame.

Fig. 28. Temperature field (K).

In Fig. 29, molar concentrations of Na_xO_y are shown. As can be observed, the region of higher concentrations is just above the sodium pool surface; nonetheless, it should be realized that location of the highest oxide concentration will depend on Na vaporization rates and O_2 supply rates, so that at high vaporization rates in O_2 -poor atmospheres, the highest oxide region might not be so close to the pool surface. Also, the Na_xO_y upward diffusion can be distinguished.

Fig. 29. Na_xO_y molar concentration (kmol/m^3).

Even though, particle generation rates heavily depend on temperatures and partial pressures, much of such a dependence is made through the saturation ratio ($S = p_{\text{vap}}/p_{\text{sat}}(T)$), which essentially indicates how high Na_xO_y vapour pressures are with respect to those at thermal equilibrium (p_{sat}). Vapour pressures of Na_xO_y are calculated from the molar concentrations by assuming ideal gas behaviour. In order to focus on the region of interest (active volume), a criterion has been adopted: sodium-oxide vapour pressure must be higher than the saturated-vapour pressure of sodium oxides at the boiling temperature (1153 K).

Due to the extremely low values of the saturated-vapour pressure of the oxides, large values of S are found in the analysed region; it is worth highlighting the large gradients of S found, with values from 10^4 to $1.6 \cdot 10^{20}$ (Fig. 30). Maximum partial pressures are reached in the flame region; more specifically, just above the pool surface. On the other hand, saturated-vapour pressure is an increasing function of temperature. Therefore, the lower S values are reached just above the pool surface. In this region, in spite of the large concentrations of Na_xO_y , the large values of saturated-vapour pressures due to the large temperatures dominate the saturation ratio. In the region near the pool centre ($x=0.010$), just above the pool, the saturation ratio slowly decreases up to 0.01 m height due to the

decrease in the molar concentrations. Above this distance over the pool, a decreasing trend in the saturation ratio is observed due to both factors: on the one hand the decrease of molar concentration and then of partial pressure; on the other hand, the temperature increase at 0.02 m height above the pool centre.

Fig. 30. Saturation ratio map at the analysed region.

Finally, Fig. 31 shows the particle concentration in the active volume (i.e., the region in which the saturation ratio is above 1.0) obtained by integration over time of the nucleation rate in all the cells forming the active volume. As expected, the highest particle concentration is found in the flame region, and more specifically, just above the pool surface. This is due to the high Na_xO_y partial pressures right above the pool in relation to the high temperatures also reached in that area (saturation pressure is an increasing function with temperature). By summing the particle concentration for all the cells, huge concentrations of particles are produced during a sodium pool fire, of the order of 10^{26} particles for this scenario and the characteristic time to attain equilibrium would be of the order of 10^{-7} s. At such high concentrations, the usual consideration that particle concentrations are dilute allowing aerosol models to assume independent gas and particle phases breaks down; strictly, the classic approximation should be abandoned since things

such as the effective density of the gas-particle phase and the turbulence itself are changed.

As noted in the graph, in less than 10 cm of height over the Na pool, the particle generation rate reduces to less than 10% of the maximum intensity. This means that in SFR containments particle generation from pool fires would be a sort of local phenomena practically restricted to a small region over the pool. Out of this region (the active volume), unrealistic values of S prevent the particle generation calculation. This observation is highly relevant for a future adaptation of the PG model to a SFR safety simulation code as ASTEC-Na (Girault et al., 2015) since, to a good approximation, particle generation can be confined to a relative small containment volume right above the Na pool surface.

Fig. 31. Particle concentration map ($\text{particles}/\text{m}^3$).

The primary-particle size distribution is presented in Fig. 32. Primary particles present very small diameters hardly reaching the nano-range in a sharp distribution in which most particles fall between $6.5 \cdot 10^{-10}$ m and $8.7 \cdot 10^{-10}$ m for the scenario proposed here. These values are consistent with the embryos sizes reported in NEA-CSNI (1979). While increasing superstation reduces critical-particle size, and in our problem high

supersaturations occur, this very small size implies clusters are stable when corresponding to just a few Na_2O molecules.

Fig. 32. Primary particle size distribution.

3.3.2.2. Parametric study of the PG model

A parametric study has been developed to analyse the influence of the main variables physically related to the governing phenomena in the anticipated scenario: pool diameter (from 0.1 m to 10 m), as the characteristic system dimension for natural convection and pool temperature (from 850 K to 1000 K), main driver for the Na evaporation from the pool. In all the cases, ambient normal conditions are considered. Table 9 synthesizes the discrete values selected to build up a total of 32 cases.

Table 9. Tests matrix

Key Variable	Range	Cases
Pool diameter	From 0.1 m to 10 m	0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 7.5, 10.0
Pool temperature	From 850 K to 1000 K	850, 900, 950, 1000

The dependencies of the calculated total number of particles (N) with sodium pool temperature and sodium pool radius (the macroscopic variables defining the scenario) for all the foreseen scenarios are analysed in Figs. 33 and 34. From the figures, it can be observed that the number of generated particles hardly depends on pool temperature (Fig. 33; however, a simple potential correlation with $R^2 > 0.99$ could be found for the dependence of N with sodium pool radius (Fig. 34).

Fig. 33. Particle number vs. Na-pool temperature.

Fig. 34. Particle number vs. Na-pool diameter.

3.3.3. Impact of agglomeration in the PG model

PG model predicts large concentrations of small particles in the close vicinity of a pool. Furthermore, a high level of turbulence is calculated in this area with turbulent-energy dissipation rates of the order of tens $\text{J.kg}^{-1}.\text{s}^{-1}$. In these conditions, turbulence-induced particle agglomeration could lead to a reduction in the total number of particles and to an increase in the average size (Friedlander, 2000). Therefore, it is necessary to evaluate the impact of agglomeration (turbulent and Brownian) on PG model estimates. Two possibilities are envisioned depending on the characteristic time of agglomeration compared to the particle-generation one: the first one is that particle generation takes place on a much faster timescale than agglomeration and the PG model does not need in this case to include agglomeration phenomena; the second one is that both particle generation and agglomeration occurs on similar timescales, then PG model would need to include the influence of agglomeration.

To evaluate the impact of agglomeration in the PG model, the characteristic times of both Brownian and turbulent agglomeration are calculated for the proposed scenarios in Table 9 by the equation:

$$t_c = \frac{2}{C \cdot \beta} \quad (34)$$

where C is the particle concentration predicted by the PG model and β is the collision frequency function or kernel (m^3/s).

In the free molecular regime, the Brownian agglomeration kernel can be calculated by (Friedlander, 2000):

$$\beta_{\text{Brownian}} = \left(\frac{3}{4\pi}\right)^{1/6} \cdot \left(\frac{6k_B T}{\rho_p}\right)^{1/2} \cdot \left(\frac{1}{v_i} + \frac{1}{v_j}\right)^{1/2} \cdot (v_i^{1/3} + v_j^{1/3})^2 \quad (35)$$

where the subscripts i, j denotes particle classes.

For the turbulent agglomeration, the collision-frequency function is calculated by considering the shear and inertial effects (SNL, 2015):

$$\beta_{\text{Turbulent}} = c_s \cdot (\beta_{\text{Shear}} + \beta_{\text{Inertial}})^{1/2} \quad (36)$$

where the shear effect is due to the relative movement of particles by their different velocities in the eddies (Saffman and Turner, 1956; SNL, 2015):

$$\beta_{\text{Shear}} = \left(\frac{\pi \cdot \varepsilon_T \cdot \rho_g}{120 \cdot \mu}\right)^{1/2} \cdot (\gamma_i \cdot d_i + \gamma_j \cdot d_j)^3 \quad (37)$$

and the inertial effect is due to the relative motion of particles by their different mass:

$$\beta_{\text{Inertial}} = \frac{0.04029 \cdot \rho_g^{1/4} \cdot \varepsilon_T^{3/4}}{\mu^{5/4}} \cdot (\gamma_i d_i + \gamma_j d_j)^2 \cdot \left| \frac{\rho_{pi} C_i d_i^2}{\chi_i} - \frac{\rho_{pj} C_j d_j^2}{\chi_j} \right| \quad (38)$$

As can be observed, these equations rely on the turbulent energy dissipation rate (ε_T) whose value has large uncertainties and greatly depends on the conditions evaluated. For example, the default value for the containment atmosphere during a severe accident of a water-cooled reactor in the MELCOR code (SNL, 2015) is $10^{-3} \text{ m}^2/\text{s}^3$. However, $\varepsilon_T \sim 10$ is predicted in the flame region just above the pool surface in the developed numerical simulation.

The characteristic times for Brownian and turbulent agglomeration are calculated at the given conditions in each scenario of the test matrix (Table 9). In this calculation, the collision of two particles has been considered where one of these particles has a diameter two times larger than the other one. In Fig. 35, the calculated characteristic times as a function of the corresponding particle concentration is presented. As can be observed, characteristic times of turbulent agglomeration (from 10^3 s to 10^8 s approximately) much longer than predicted times for particle generation (10^{-7} s , dotted black line) are obtained; hence, turbulent agglomeration should not affect PG model estimates. However, characteristic times for Brownian agglomeration are longer than the particle generation times until scenarios with concentrations larger than 10^{22} particles (small pool scenarios). Hence, in the case of small pools with diameters less than 0.1 m , Brownian agglomeration could affect the PG model results.

Fig. 35. Characteristic times vs. particle concentration.

3.4. Chapter summary

This chapter presents the main features and bases of a phenomenological Particle Generation model (PG model) developed to bringing the currently existing gap in integral severe accident codes from primary particle formation to final particle behaviour.

The developed PG model covers sodium-vapour burning and formation of sodium aerosols above an evaporating sodium pool. As final result, this model offers the sodium-oxide particle generation rate and the primary particle size.

The PG model is the result of articulate a set of individual models for covering sodium-vapour burning and formation of sodium aerosols above an evaporating sodium pool: Na vaporization, O₂ transport by air natural circulation, Na-O₂ chemical reactions and vapour-to-particle conversion of Na-oxides.

Its consistency has been partially validated by comparing with available experimental data. Predictions from the model include large temperature and vapour concentration gradients set over the sodium pool which result in very high particle concentrations in the close vicinity of the pool.

Chapter 4

Zero-D PG MODEL DEVELOPMENT

As shown in the previous chapter, particle generation from a Na pool fire is associated with substantial gradients of temperature, Na_xO_y vapours and oxygen concentrations as well as turbulent agitation in the region right over the thin reaction layer set up next to the pool surface. A detailed picture of the scenario looked mandatory to achieve a thorough understanding of the physic-chemical scenario set. Nevertheless, using 3D computational fluid-dynamics in analysis of Beyond Design Basis Accidents (BDBA) seems presently unsuitable, due to the lack of validation of these tools in the domain of SFR safety, and impractical, since the necessary computing resources and the number of scenarios to be explored would turn this approach far too onerous. As a consequence, the codes presently under development to address these scenarios do adopt a lumped-parameter approach. In other words, in order to turn the PG model described in the previous chapter into a useful analytical tool to be used in these codes, a 0D version had to be built up.

In order to turn the 3D model chosen into a 0D consistent version, some qualitative criteria have been adopted:

- The 0D response to major environmental variables (i.e., pool temperature, oxygen concentration, over-pool gas velocity and composition, etc.) should follow the same trends shown by the original 3D model;

- The quantitative deviations of the 0D predictions with respect to the 3D estimates should be within the uncertainty range of the latter in the main output variables of the model (i.e., particle generation rate and primary-particle size distribution);
- The final formulation of the 0D model should be compatible with architecture and variables available in integral lumped-parameter codes to be used for SFR severe accident analyses (i.e., MELCOR-Na and/or ASTEC-Na).

4.1. Zero-D PG model

4.1.1. Fundamental equations

In addition to the qualitative criteria introduced above, the 0D adaptation of the PG model is based on the preservation of the total number of generated particles formed in the active nucleation volume (i.e., the region over the pool in which Na-oxides are supersaturated):

$$N_{3D} = \sum_i \left(\int_{\Delta t} J_i^{CNT} (T_i, p_{v_i}) \cdot dt \right) \cdot v_i \equiv N_{0D} = \left(\int_{\Delta t} J^{CNT} (\bar{T}, \bar{p}_v) \cdot dt \right) \cdot V_{PG} \quad (39)$$

In this equation (Eqn. 39), the number of generated particles (N_{3D}) in the active volume is given by the integration over time of the nucleation rate in all the cells forming the active volume (summation running over subindex i). As shown at the right side of the equation, the 0D approximation means to find out a characteristic nucleation rate that keeps the major CNT dependencies and relies on average gas properties ($\bar{T}, \bar{p}_v$) of the entire active volume:

$$N_{0D} = \left(\int_{\Delta t} \left[\left(\frac{2\sigma}{\pi m_l} \right)^{1/2} \cdot v_l \cdot \bar{N}_l^2 \cdot \exp \left(-\frac{16\pi}{3} \cdot \frac{v_l^2 \sigma^3}{(k_B \bar{T})^3 (\ln \bar{S})^2} \right) \right] \cdot dt \right) \cdot V_{PG} \quad (40)$$

$$\bar{T} = \frac{1}{V_{PG}} \sum T_i \cdot v_i \quad (41)$$

$$\overline{p_v} = \frac{1}{V_{PG}} \sum p_{v_i} \cdot v_i \quad (42)$$

$$\overline{S} = \frac{\overline{p_v}}{p_{sat}(\overline{T})} \quad (43)$$

As in Eqn. (40), the critical particle size of the 0D adaptation is calculated on average gas conditions:

$$d_{0D} = \frac{2\sigma v_1}{k_B \overline{T} \ln \overline{S}} \quad (44)$$

Then, the growth by condensation is accounted for by the removal of vapours by condensation as the net flow of molecules attached to the surface of the particles generated by homogeneous nucleation.

4.1.2. The model assessment

Given the absence of experimental data on particle generation from sodium pool fires, a theoretical case matrix has been set up as an engine to build an analytical database resulting from the 3D model running under the scenarios outlined. The cases have been characterized by variables physically related to the governing phenomena in the anticipated scenario: pool diameter (from 0.1 m to 10 m), as a characteristic system dimension for natural convection over the pool; pool temperature (from 850 K to 1100 K), as the main driver for the Na evaporation from the pool; oxygen concentration (from 21% down to 1%), as a reactant which might potentially limit the conversion of Na into Na_xO_y . Table 10 synthesizes the discrete values selected to build up a total of 200 cases.

Table 10. Tests matrix (see Appendix D).

Key Variable	Range	Cases
Pool diameter (m)	0.1 – 10	0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 7.5, 10.0
Pool temperature (K)	850 – 1100	850, 900, 950, 1000, 1100
O ₂ content (%)	1 – 21	1, 5, 10, 15, 21

Some of the cases calculated have been screened out due to different reasons. Cases with 1% O₂ have been dropped from the matrix because homogeneous nucleation conditions are not met (a total of 40 cases dismissed). A check of mass balance consistency has been conducted to make it sure that the 3D model does not artificially produce particles richer in Na than what the pool vaporization rate would allow; this second conditions entailed to drop 28 more cases from the matrix. Thus, in total the analytical case matrix consisted of 132 cases.

The calculated total number of particles by the PG model (N_{3D}) versus the total number of generated particles from the 0D adaptation (N_{0D}) for 132 scenarios is shown in Fig. 36 (some areas of the plot have been amplified for an easier observation). As observed, the total number of particles ranged between 10^{18} and 10^{24} for any of the O₂ concentrations considered, so that a broad interval of particle number has resulted from the cases considered in the matrix. It is worth noting that both approaches agreed in the order of magnitude of particles formed, experiencing an average deviation of around 4% (never exceeding 15%).

Fig. 36. N_{0D} vs N_{3D} .

In the 0D PG model, all the particles are generated under the same average conditions for a given scenario so that the growth rate is identical for all the particles. This prevents from a strict quantitative comparison between the 3D approach and the 0D one, but a qualitative comparison still makes sense. Fig. 37 shows that primary particle size extends from around $7.0 \cdot 10^{-10}$ m to $1.2 \cdot 10^{-9}$ m in both approaches despite the absence of distributions in the 0D model. In the PG model (Fig. 37 (a)), primary particle size is calculated by considering a single burst of homogeneous nucleation (critical size). From this point on, particle growth is controlled by condensation, which in turn depends on boundary conditions. Oxygen concentration has been noted to have a noticeable impact in the particle size distribution: the higher is the oxygen concentration, the higher is particle number and the smaller is particle diameter. Namely, high oxygen concentration enhances formation of Na_xO_y so that vapour pressure increases and nucleation rate is fostered at smaller critical particle size. Consistently, the 0D approximation estimates smaller sizes for higher O_2 concentrations (Fig. 37 (b)).

Fig. 37. Primary particle diameter.

In summary, the 0D model adaptation has been shown to succeed in meeting the two quantitative criteria set in terms of number of particles and primary particle size.

4.2. Zero-D correlations

Some of the variables embedded in Eqns. (39) and (43) might not be available in lumped parameter codes used for severe accident analysis of SFRs (N_1 or $\bar{S}$, for example). By exploring the sensitivity of the model to variables governing dominant processes (as stated in Table 10), the physical consistency of the 0D model may be confirmed and the key model trends stated. They will be the pillars for the 0D correlation proposed below, which architecture will allow a straightforward implementation within severe accident system codes, like ASTEC-Na.

Fig. 38 and Fig. 39 present the N_{0D} model trends with Na vaporization rate and oxygen fraction. Fig. 38 shows a sound linear trend (drawn in black) of the number of particles with the Na-vaporization rate, although there is a substantial scattering (1- 2 orders of magnitude) at any Na-vaporization rate that accounts for other variables influence. Such an increase is what expected since the more Na vapour is made available, the higher number of particles might be formed. Fig. 39 displays the growing trend of the number of particles with the oxygen concentration at each pool dimension (Fig. 39(a)) diameter and temperature (Fig. 39(b)); in addition, two more insights may be drawn from the plot: a stronger correlation of N_{0D} with O_2 fraction than with Na-vaporization rate (i.e., higher sensitivity of N_{0D} to X_{O_2}) and the much larger scattering caused by other variables. In order to better illustrate the influence of pool diameter and temperature, Fig. 40 plots

the specific variations of N_{0D} with both variables in the 21% O_2 scenario (the rest of cases showing the same trends). In short, whereas T_{pool} slightly affects the number of particles in the range explored, d_{pool} changes make a quite noticeable effect that might fit a potential relation with N_{0D} .

Fig. 38. N_{0D} as a function of Na-vaporization rate.

Fig. 39. N_{0D} as a function of O_2 concentration.

Fig. 40. N_{0D} variation as a function of T_{pool} and d_{pool} for the 21% O_2 scenario.

As for the primary particle diameter trends with main variables, the study is further simpler due to the small sensitivity shown by the model (range between $7 \cdot 10^{-10}$ and $1.2 \cdot 10^{-9}$ m). Hardly any variation has been found as a function of T_{pool} and d_{pool} , whereas oxygen concentration clearly shows an inverse relation between both variables (Fig. 41): the higher O_2 concentration, the smaller the particle primary size. This trend is again consistent with the fact that higher Na_xO_y vapour pressures translate into smaller primary sizes according to the Classical Nucleation Theory (Becker and Döring, 1935; Farkas, 1927; Zeldovich, 1942).

Fig. 41. $d_{p,0D}$ as a function of oxygen fraction with pool diameter (m).

Based on the individual trends presented above, N_{0D} has been linearly correlated with the vaporization rate and potentially correlated with the pool diameter and the pool temperature:

$$N_{crlm} = 7.8478 \cdot 10^{26} \cdot \dot{m}_{Na} \cdot d_{pool}^{0.22} \cdot X_{O_2}^{3.03} \quad (45)$$

Fig. 42 displays the correlation predictions vs. those from the 0D model. Correlation shows quite a good behaviour with an average relative deviation around 50%. In section 3.2.4, it has been estimated that just by considering the uncertainties affecting the physical properties intervening in the nucleation modelling a 2-orders of magnitude uncertainty band should be anticipated in the calculation of particle number. Therefore, the deviations incurred by the correlation proposed are acceptable.

Fig. 42. Particle generation rate (correlated vs. 0D PG model results).

Given the narrow interval found by the 3D model concerning primary particle diameter ($7.0 \cdot 10^{-10} - 1.2 \cdot 10^{-9}$ m), to derive an accurate correlation is not that important. Nonetheless, the weak dependencies on pool diameter and temperature and the stronger decreasing effect of O_2 concentration observed above, have been encapsulated in the following expression:

$$d_{p_{critn}} = 1.5913 \cdot 10^{-10} \cdot d_{pool}^{0.0239} \cdot \ln\left(\frac{1}{X_{O_2}}\right) \cdot \frac{1}{T_{pool}^{0.2281}} \quad (46)$$

In Fig. 43 the primary particle diameter given by the correlation is compared with the primary particle size by the 0D PG model; even though the correlation tends to underestimate the model predictions, the absolute average relative deviation is less than 18 %. Anyway, the narrow diameter interval and the presumable uncertainties affecting any calculated size, make a primary particle diameter of $10^{-3} \mu m$ a reasonable assumption for Na-based particle generation modelling.

Fig. 43. Primary particle diameter (correlated vs. 0D PG model results).

4.3. Chapter summary

In order to turn the PG model described in the previous chapter into a useful analytical tool in the current context of lumped-parameter codes in the SFR safety domain, a 0D version has been build up.

This chapter presents the adaptation of the 3D global PG model to a 0D model based on the generation of particles under average system conditions. For consistency purposes, the adaptation has been supported on three qualitative criteria. In addition to these, the preservation of the total number of generated particles formed has been guaranteed.

Deviations between both approaches less than 15% have been found in all the simulated scenarios (a total of 132 cases covering different scenarios). From the 0D model, simple correlations for the amount of particles generated and primary particle size relying on Na vaporization rate, Na-pool dimension, temperature and O₂-concentration have been derived into a form ready to be implemented in any lumped-parameter code. Its right performance has been tested against more than 100 comparisons with the original 3D model with successful outcomes.

Chapter 5

PG MODEL VALIDATION

5.1. Introduction

In the frame of the EU JASMIN project, a code extension to the containment thermal-hydraulic and aerosol model of the ASTEC code, CPA, has been developed to enable first capabilities to simulate sodium pool fires. As a result, a new version of the ASTEC module addressing in-containment accident evolution has been built by including models highly parametrized for sodium fires coming from SOFIRE (Beiriger et al., 1973) and models genuinely produced within the project for the primary particle generation (subject of this thesis work) and for the chemical ageing of sodium-oxides particles (Mathé et al., 2015). The resulting version of CPA is hereafter referred to as CPA*.

In this chapter, an overview of the implementation of the PG model correlations within the ASTEC-Na CPA code is presented. Prior to its implementation, a feasibility analysis was developed (see Appendix F). At this point it should be clarified that, in the frame of the JASMIN project, CIEMAT has been carried out the theoretical model development for particle generation but not its implementation in ASTEC-Na. A general description of the implementation is given in this chapter to offer the full picture of the developed work and for a better understanding of the results.

Besides, this chapter presents and discusses the assessment of the extended code version against experimental data and the major findings of the data-estimates comparison will be given.

5.2. Implementation of Zero-D correlations in CPA*

The new CPA version (CPA*) includes two options for the particle production from sodium pool fires: a sodium pool fire model based on the SOFIRE code formulation (Beiriger et al., 1973) in which sodium burning rate is limited by the diffusion of oxygen into the pool (surface reaction) and particle generation is assumed as infinitely fast or immediate; and the correlations derived from the 0D adaptation of the PG model, which is based on Na vapour gas-phase reactions (flame sheet approach) and the particle formation kinetics according to the Classical Nucleation Theory and the subsequent vapour condensation onto particle seeds.

The implementation of the correlations proposed in Eqns. (45) and (46) demands some additional information, like the sodium vaporization molar flow rate (assuming a diffusion layer approach):

$$\dot{m}_{Na} = \frac{D_{Na} \cdot X_{Na} \cdot C_{bl} \cdot \ln\left(\frac{P}{P - p_{sat,Na}}\right) \cdot A_{pool}}{l_f} \quad (47)$$

where the flame temperature (T_f) needed to estimate D_{Na} and C_{bl} as well as the distance from the pool surface to the flame (l_f) are given by correlations obtained from the tests matrix (Table 10):

$$T_f = T_{pool} + 1397.13 \cdot X_{O_2} \quad (48)$$

$$l_f = 1.061 \cdot 10^{-16} \cdot \frac{1}{X_{O_2}^2} \cdot \exp(0.026163 \cdot T_{pool}) \quad (49)$$

The oxygen mass flux is calculated by assuming equal generation rates of the two Na-oxide species considered (Na_2O and Na_2O_2):

$$\dot{m}_{O_2} = X \cdot \dot{m}_{Na} \cdot M_{Na} \quad (50)$$

where X is the oxygen-sodium stoichiometric ratio.

The conversion from Na-particle number to mass is conducted by assuming that particles formed can be approximated as spheres:

$$\dot{m}_{Na,PG} = \frac{\dot{N}_{crltn} \frac{\pi}{6} d_{p_{crltn}}^3 \rho_{aero}}{1.52} \quad (51)$$

where ρ_{aero} is a constant density specified by the user for the aerosol behaviour calculations according to the multi-component aerosol approach of ASTEC CPA (Bestele and Klein-Heßling, 2000).

The generated aerosol mass of Na_2O and Na_2O_2 is then calculated by the code:

$$\dot{m}_{Na_2O} = 0.673 \cdot \dot{m}_{Na,PG} \quad (52)$$

$$\dot{m}_{Na_2O_2} = 0.848 \cdot \dot{m}_{Na,PG} \quad (53)$$

5.3. Validation test matrix

In order to assess the ASTEC-Na CPA code (CPA* up to now), a literature review of experimental information led to nearly 20 experiments related to Na fires, of which nearly half dealt with aerosol generation from pool fires. It is worth noting here that much of the experimental work carried out in the past is nowadays hard to use since in most cases no electronic record is available and information is usually found in hard technical reports.

A methodology to identify the most suitable experiments has been developed. The methodology is based on the application, by order of priority, of 5 criteria: representativeness of boundary conditions, normal test execution (no test artefacts), multiple scales, number of key variables documented in the available literature and accuracy of available data. As a result, three experiments, two from ABCOVE program (AB1, AB2) and one from FAUNA program (F2) were chosen for the assessment of CPA*. A full description of the selection process is shown in Appendix G. As a result, attention was paid to specific tests of the ABCOVE and FAUNA programs, a description of which is given below.

The ABCOVE experiments were conducted in the Containment System Test Facility (CSTF) vessel at the Hanford Engineering Development Laboratory in the United States. The containment was a cylindrical steel vessel (7.6 m diameter, 20.3 m high) of about 853 m³ (Fig. 44). The vessel was furnished with instrumentation to monitor both thermal-hydraulics and aerosol behaviour. In these tests, the experimental arrangement included ten clusters of filter samples at various locations throughout the vessel atmosphere, each cluster containing 12 filters; four Thief sample stations: the types of samples taken included filter samples for mass concentration measurements, samples for chemical species identification, deposition coupons and cascade impactors for particle size measurements; and two gas sample systems that provided on-line analysis of oxygen, moisture and hydrogen concentration (one taking gas from high in the atmosphere and one from low in the vessel). A more thorough description of experimental aspects may be found in Hilliard et al. (1979, 1977); McCormack et al. (1978); Souto et al. (1994).

Fig. 44. CSTF Vessel arrangement.

The ABCOVE programme conducted a total of 7 experiments related to Na fires and airborne aerosols, but only three of them were pool fire experiments (AB1, AB2 and AB7). Unfortunately, an experimental artefact in the AB7 execution prevented its use for validation purposes.

In test AB1 (Table 11), 410 kg of sodium at 600 °C was spilled into a burn pan of 4.4 m² through an electrically heated delivery line. The burn pan had a hinged lid which was in the vertical position during the spill. The sodium flow lasted 80 s and the splashing was minimized by baffles in the pan. At 60 min after the initiation of the spill, the lid was closed and the sodium pool fire extinguished.

The AB2 test was performed with essentially the same initial conditions (Table 11), but with the addition of an injection of steam, at a rate of 0.02 kg/s, near the centre of the containment vessel for 60 min beginning 16 min after the start of the fire. The steam injection was meant to simulate the release of water vapour from heated concrete at a rate equivalent to the release of water vapour from ~ 10-30 m² of hot concrete (at a ratio of 1.0

kg H₂O per kg of aerosol). In this test, 472 kg of sodium at 600 °C were delivered and the pool fire burn duration was 60 min.

The FAUNA facility consists of a fire room, a measuring room, and an aerosol measuring loop. A cylindrical steel vessel of 6 m in diameter and 6 m high with domed ends (volume 220 m³) served as the fire room (Fig. 45) with all the instrumentation needed to monitor both thermal-hydraulics and aerosol behaviour. Inside the FAUNA containment vessel, sodium pool fire was produced in a circular burning pan. Closely above the burning area a hood was placed in order to draw aerosols into the measurement loop. At these sample ports mass concentration of aerosol was determined by filter probes and size distribution by impactors. Additional filter probes were taken for the wet chemical analysis (Cherdron et al., 1990; Cherdron and Charpenel, 1985; Cherdron and Jordan, 1983, 1980).

Fig. 45. FAUNA aerosol loop (Cherdron et al., 1985).

A total of 13 tests were conducted in the FAUNA facility, 7 of which (F1-F7) investigated pool fires. The F2 test was chosen to complete the set of experiments to be used in the code assessment due to the different scale compared to ABCOVE, the thorough reporting of data and the absence of any kind of experimental artefact that might affect results.

In the F2 test (Table 11), a sodium pool fire was produced inside the FAUNA containment in a circular burning pan of 1.6 m diameter ($\sim 2 \text{ m}^2$) by the release of 250 kg of sodium at 500 °C for more than 3 h (210 min). During the experiment, the oxygen content was kept constant through 3 injections of approximately 1% of the vessel molar content with different duration.

Table 11. Summary of tests conditions.

	AB1	AB2	F2
Geometry			
Type	Cylindrical	Cylindrical	Cylindrical
Volume (m^3)	852	852	220
Initial Conditions			
O ₂ (%)	19.8	20.9	17-25
Temperature (K)	299.65	293.65	298.15
RH (%)	35.5	43.3	-
Steam Addition	NO	YES	NO
Sodium Spill			
Initial Na Temp. (K)	873.15	873.15	773.15
Burning Area (m^2)	4.4	4.4	2
Fire duration (s)	3600	3600	12600

5.4. Modelling of the experiments

5.4.1. Nodalisation and heat structures

AB1 and AB2 calculations share the same nodalisation: a single cell (852 m³). Six walls for heat transfer and aerosol deposition representing the top and bottom heads, the cylindrical wall, the internal components for aerosol plating and settling and the sodium pool surface, have been considered. For all the walls, the material facing the vessel atmosphere was stainless steel. Vessel walls are insulated from the outside with a 2.54 cm layer of fiberglass. The sodium pool surface has been modelled as a 4.4 m² hot structure facing the gas atmosphere.

The nodalisation of the FAUNA vessel consists of one node (220 m³). Four walls (top and bottom heads, cylindrical wall and sodium pool) have been considered for heat transfer and aerosol deposition. The vessel walls (top, bottom and cylinder walls) have been modelled as made of stainless steel (1.6 cm of thickness). As no accurate information on the vessel insulation has been found, thermal insulation is simulated imposing adiabatic conditions at the bottom head and constant external temperature (313.15 K) at cylindrical walls and upper head. As in ABCOVE models, the sodium pool has been modelled as a rigid structure (2 m²).

5.4.2. Aerosol modelling

CPA* new models estimate the amount of Na₂O and Na₂O₂ particles being produced as a function of time. Primary particle size is calculated in CPA* through the PG model correlation (Eqn. 46) and then allows particles to agglomerate; a lognormal distribution has been assumed in all the cases.

Additionally, aerosol coefficients in CPA* are set in the input deck (i.e., shape factors, conductivity, etc.). For them, default values have been used. Regarding aerosol density, this has been estimated as a function of Na₂O and Na₂O₂ distribution (2800 kg/m³) (Table 12).

Table 12. Aerosol coefficients and density (for all the tests).

Aerosol coefficient	Value
χ	1.00
γ	1.00
F_{slip}	1.37
STICK	1.00
ε	0.02
$k_{\text{gas}}/k_{\text{p}}$	0.03
c_t	1.00
ρ (kg/m ³)	2800

5.5. Prediction/data comparison

A thorough description of data evolution and behaviour of CPA* predictions are reported here, focused on the code performance with the PG correlations (CPA*_PG). The other calculation option is also included (CPA*_SOFIRE).

Comparison of CPA* to data are shown below in terms of atmosphere temperature, pressure, airborne aerosol concentration and size as a function of time, and final Na distribution among walls.

In order to assess the model implementation adequately, a previous discussion on the uncertainty associated to the experimental data is included before the discussion itself. Two aspects can be distinguished: the local/average nature of the experimental data and the uncertainty associated to the data extraction process.

The local/average nature is directly related to their significance as representative of the whole scenario (as local values of some variables could not give a meaningful indication of the governing phenomena) and to the credit that data-estimates comparisons should be given in terms of validation (i.e., comparison of a local gas temperature with the gas temperature prediction of a single node calculation for a vessel of hundreds of m³ might be meaningless). The uncertainty associated with the data extraction process can be crucial: a numerical value taken from a text or table in a scientific/technical report can be assumed to be “as given”, whereas if data are taken from figures the extraction accuracy

will be dependent on the quality of the plot, the type (linear vs. log), the tool used to pick the data points, etc.

5.5.1. Thermal-hydraulics

Thermal hydraulics are analysed through the comparison of experimental data on atmosphere temperature and atmosphere pressure.

Data analysis

In the AB1 and AB2 tests, the experimental temperature is the mean value of 8 thermocouples from high, low and central regions in the containment atmosphere at different azimuthal locations and distances from the centre. The maximum standard deviation of average temperature is below 5% in both tests (Hilliard et al., 1977). All the values have been taken from tables, so no error should be attributed to the data extraction process. Therefore, data-code comparison can be set and given credit whenever the experimental errors are taken into account.

As for pressure, any local measurement can be reliable for comparison with single-cell estimates and no error has been made in the extraction process since data have been taken as numerical values from a table.

In the F2 test, the two local temperatures at the same axial location (around 4 m above the pan base) and the two radial positions that cover all the local measurements have been considered for comparisons. Given the shortage of information at other locations, particularly at different heights and radii, the comparison to a “cell temperature” estimated by codes should be done in terms of trends and physical reasonableness. Additionally, some errors should be associated to the extraction process as data were taken from a figure (Cherdron et al., 1990) in which the broad scale in temperatures and time would allow absolute errors of 10 K and 60 s, respectively.

Results and discussion

Atmosphere temperature and pressure for AB1 and AB2 tests are shown from Fig. 46 through Fig. 50. From the figures, the same experimental evolution can be observed. Experimental gas temperature evolution may be described in two main phases: heat-up and cool-down. The heat-up phase is, in turn, split into 4 stages: a first period (about 60 s) in which a sharp increase of temperature occurs: “fresh Na” reacts without any major kinetic resistance; a second one along which temperature hardly changes for about 500 s; a third one in which temperature increase proceeds gently for some 2000 s; and a last period until the fire quenching, where heat-up slightly slows down. A possible explanation is that

Na pouring into the experimental pan entails a large surface-to-volume ratio of so-called “fresh Na”, which is eager to react without any major kinetic resistance than the one associated to O₂ availability.

Once in the pan, several factors might slow down Na-O₂ chemical reactions as the decrease of the Na surface/volume ratio or the slowing down of the Na vaporization rates due to the absorption by the pan of the Na thermal energy. Besides, as the pool surface temperature decrease, Na-O₂ gas phase reactions above the pool surface become surface reactions on the pool surface, which introduces a major kinetic resistance.

The cooling down shows two stages: a fast one due to chemical reactions brought to a halt and the isolation of the hot sodium by covering the burn pan, and a longer and more progressive one, as heat is steadily lost to the vessel walls principally by natural convection.

This profile is somewhat distorted in the case of the F2 experiment (Fig. 50) for two main reasons: the F2 atmosphere was not well mixed during Na burning and temperature at the central axis of the vessel ($x = 0.0$ m) became highly sensitive to O₂ concentration, so that whenever O₂ concentration decreased temperature fell down noticeably; in addition, even though the fire end was set at 12600 s in the test protocol, according to temperature data, fire was progressively extinguishing from around 6000 s, which might be caused by a slow supply of O₂ by the convection loops set in the vessel with respect to the Na burning rate at the measurement locations. As O₂ concentration is far from being zero in the vessel at 6000 s, the temperature trend might mean that it takes some time for O₂ at other locations than the burning pan vicinity to reach it or, in other words, that Na burning is much faster than convection loops set in the vessel as a consequence of Na burning.

As observed in Fig. 46 to 50, estimates and data roughly follow the same thermal trends by describing a heat-up phase, in which Na oxidation is taking place, and a cooling phase, in which Na fire extinguishes and a fast cooldown period right after the fire is over, is followed by moderate cooling governed by natural convection. As for the specific CPA*_PG behaviour, it closely captured the first 500 s of Na fires (AB1 and AB2 tests), but then it underestimated data during the heat-up phase. This might indicate that either more chemical energy should have been released or a larger fraction of the chemical energy produced should remain in the atmosphere. Given the validation of the 3D PG model in terms of burning rate with Newman’s data and the assumption of instantaneous chemical reaction, this might indicate a slight underprediction of the Na vaporization rate when converting Eqn. (47) into an adapted version for lumped-parameter codes. However, the similarity of the CPA*_SOFIRE slope during most of heat-up phase indicates that this is not strictly linked to the PG adaptation modelling (the apparently closer agreement of

CPA*_SOFIRE with data at later times during the heat-up phase coming from the noticeable overprediction in the first 500 s of the test). During the cooling phase, the CPA*_PG behaves similar to data, although the fast temperature decrease right after Na fire is slightly more moderate possibly due to the smaller temperature differences with surrounding heat structures as a consequence of the underestimate of gas temperature during the heat-up phase.

In F2, the experimental footprint is not captured by predictions, in which the fire end was set to happen at 12600 s. On the other hand, the single-cell approach prevents CPA* code from capturing any sort of O₂ scarcity at the fire location.

Fig. 46. Atmosphere temperature in AB1.

Fig. 47. Pressure (AB1).

Fig. 48. Atmosphere temperature in AB2.

Fig. 49. Pressure (AB2).

Fig. 50. Atmosphere temperature in F2.

5.5.2. Aerosol behaviour

Much more closely related to the PG modelling are the evolution of airborne aerosol concentration and size. A lot of aerosol related data were collected in the experiments. The three main metrics used in the code assessment are the suspended mass concentration, the Aerodynamic Mass Median Diameter (AMMD), and the mass distribution at the end of the tests.

Data analysis

In the AB1 and AB2 tests, the experimental suspended mass concentration is the average of 4 locations from high, low and mid regions in the vessel and the data are available as tables in Hilliard et al. (1979). As noted in the figures below, the standard deviations at sometimes are substantial, so that any data-code comparison should be done with caution, particularly during the aerosol generation phase of the experiments.

The average AMMD measurements were taken at high and low containment locations and they show noticeable consistency. It is noteworthy that the first data point available is around 1000 s, so that the time gap since the fast Na-injection transient has been long enough to reach a reasonable degree of uniformity in the vessel. Thus, from the aerosol perspective, any data-code comparison seems reasonable even under the well-mixed atmosphere hypotheses made in the calculations. Nonetheless, taking data points from a log-log plot results in extraction uncertainties that have been postulated to be dependent on the relative position of the data points with respect to the beginning of the order of magnitude (OM) in the log scale: 0.1 OM, if data are near the mark of the OM in the plot; and 1.0 OM, if data are closer to the next OM. This approximate way of estimating uncertainty ranges is the basis of the ones shown in the figures below.

The distribution of deposited sodium is taken from tables. According to these tables, only the deposited sodium on the bottom and the safety catch pan and personnel deck come from measurements. The rest of the values are calculated (Hilliard et al., 1979).

For the F2 test, local measurements have been taken for both concentrations and AMMDs. There is no experimental evidence, as in the ABCOVE tests, that the facility atmosphere was well-mixed, so any local magnitude cannot be taken as representative of the whole facility. In addition, concentration data points in the plot have been taken by selecting specific spots along a continuous curve in a log-log plot. As for uncertainties associated with data points, the same criteria as the ones defined above for ABCOVE have been used for concentrations, in which both axes are in log scale (Cherdron et al., 1985). AMMDs measurements were derived from samples taken closely above the burning area (i.e., approximately 200 s aging), so that they cannot be said to be representative of particle sizes in the entire vessel; the data points have been taken from a linear-linear plot.

Results and discussion

Fig. 51 shows the evolution of the aerosol concentration in AB1 test. Large uncertainties associated with the experimental data can be observed before 1000 s. During the burning phase (0-3600 s), a quasi-steady state between 0.02 and 0.03 kg/m³ was measured, so that there was a balance between particle generation and aerosol deposition; afterwards, once the Na fire is over, concentration decayed progressively. Again in AB2 (Fig. 52) it is not easy to identify a clear trend during the aerosol injection period (0-3600 s) due to the substantial associated uncertainties affecting some of the data. However, one may assume a soft growing trend from around 0.02 kg/m³ to 0.035 kg/m³. The depletion phase, although qualitative similar to AB1 one, shows an initial decay rate nearly 3 times slower. The evolution of the airborne concentration in F2 test is presented in Fig. 52. The first experimental data are approximately at 1000 s. From this time, experimental airborne concentration seems to follow a slow growth up to 6000 s and then an equally slow decrease, which is consistent with the thermal observations made above and the postulate of a reduced of Na-burning; however, when uncertainty bars are accounted for, such an experimental trend is harder to defend.

Fig. 51 through Fig. 53 present the CPA*_PG airborne concentration estimates together with data and CPA*_SOFIRE predictions for the three experiments. Due to the reasons given above comparisons to data in the case of the F2 test will be restricted to the first 6000 s. In AB1 and AB2, CPA*_PG calculations show consistency with data until around 2000 – 2500 s, along which they are within the experimental uncertainties; however, if credit is given to the blurred increasing trend (large experimental uncertainties prevent from firmly accepting that such a tendency is true), this might either support a

higher Na vaporization rate, as explained above, or indicate a too efficient particle removal by the aerosol depletion mechanisms (mainly sedimentation). Anyway, the larger deviations found with respect to data are within a factor of 2.0 (CPA*_SOFIRE estimates behaved similarly but with a shift to higher aerosol concentrations that locates them beyond the experimental uncertainties during the early times of heat-up phase). As for the F2 experiment, the CPA*_PG calculations show a growing trend consistent with data tendency for the first 6000 s, although experimentally the sharp increase predicted at the beginning of the test (and also measured in AB1 and AB2) did not exist, which is likely related to the stratified atmosphere reported in the test. Once the Na fire is over, the particle generation model has no effect on aerosol evolution, so that discrepancies with data cannot be attributed to PG modelling.

Fig. 51. Airborne concentration (AB1).

Fig. 52. Airborne concentration (AB2).

Fig. 53. Airborne concentration (F2).

Fig. 54 displays the AMMD evolution in AB1 test. The data experienced a jump from about 6 μm to approximately 8 μm between 4000 and 5000 s. This change may be attributed to the end of injection of small particles from the fire, so that naturally the size distribution shifted to bigger sizes. Then, a progressive decrease of the particle size can be observed as a consequence of preferential deposition of large particles by sedimentation.

Contrary to differences in AB2 concentration profile with respect to AB1, AMMD shows an evolution very similar to AB1, both qualitatively and quantitatively (Fig. 55), and calculations also behave the same way.

Regarding the particle size in F2 (Fig. 56), as data were taken quite close to the aerosol source, overpredicting should be the expected code behaviour, as particles with short time of flight would not have had the time to agglomerate to a good extent.

Given the absence of data before 1000 s, no discussion on predictions can be held concerning the earlier times of the heat-up phase, except for stating that particle growth predicted by both CPA* approximations are consistent with the data available (Fig. 54 and Fig. 55). This is particularly so in the AB1 test, in which a steady state is observed in the AMMD until the fire end time; contrarily, in the AB2 test, a growing trend, not estimated by any of the CPA* calculations, might have existed, although again the experimental uncertainties do not allow crediting such a trend. Anyway, the comparisons support that CPA*_PG implementation does not distort the particle growth observed at two key times: early during the heat-up phase to roughly the measured diameter and once fire is over and particle generation is not active anymore, making predictions follow the particle size jump. Regarding F2 (Fig. 56), CPA*_PG noticeably overpredicted; however, this is the expected behaviour because the measurements were made quite close to the aerosol source so that particles had a short “time of flight” (i.e., particle size practically unaffected by agglomeration processes); this explanation is consistent with data steady behaviour before and after the fire was put out, instead of drawing a size jump due to the stop of small particles injection in the vessel.

Fig. 54. AMMD (AB1).

Fig. 55. AMMD (AB2).

Fig. 56. AMMD (F2).

Fig. 57 and Fig. 58 shows the final mass distribution for AB1 and AB2 tests. Even though CPA* predictions reproduce this qualitatively, still noticeable differences are noted in magnitude. In general, it seems that predictions overestimate the importance of thermophoresis as a deposition mechanism, predicting a much higher mass fraction on walls and vertical surfaces than observed. By comparison, PG model implementation does not modify gravitational sedimentation as the main deposition mechanism.

Fig. 57. Na distribution (AB1).

Fig. 58. Na distribution (AB2).

5.6. Chapter summary

This chapter presents the implementation of the analytical correlations derived from the Zero-dimensional PG model in an integral severe accident tool (ASTEC-Na). Once implemented, the performance assessment against available large-scale separate effect tests has been undertaken.

According to the comparisons to data set, the correlations do not adversely impact the code estimates with respect to other more empirical alternative approaches and, in addition, the correlations remove any need of user-defined ad-hoc parameters in the input deck concerning Na-based particles behaviour, as other alternates do. Regarding code behaviour, the model predictions yield the same order of magnitude both in terms of suspended aerosol concentration and diameter as data and capture the reliable measured data trends.

Chapter 6

CONCLUSIONS AND FINAL REMARKS

This work thesis presents a step forward in modelling in-containment source term during potential severe accidents in Na-cooled reactors. In particular, a model for particle generation during sodium pool-fires has been developed and validated against some of the more sound available data in the open literature once implemented in ASTEC-Na CPA. From all this work the main achievements thoroughly described in previous sections are highlighted below. Finally, improvements and further investigations can be proposed as work to be carried out in the future.

Filling the gap of particle formation from sodium pool fires

During hypothetical SFRs accidents leading to core damage, it is foreseen the ejection of material in the form of liquid sodium (Na) mixed with fuel and fission products into the containment. In the presence of oxygen, combustion of Na results in the formation of huge amounts of Na-oxide aerosols that would govern the suspended radioactivity inside the containment; this together with the potential harm associated with the chemical species resulting from the Na-oxides reaction with water vapour present in the atmosphere would be responsible to a great extent for the radiological and chemical impact of any potential source term.

In the frame of a PIRT exercise on the fission product and aerosol generation and transport within a generic SFR containment during postulated BDBAs, an exhaustive review of currently available data and modelling capabilities of in-containment source term analysis in accident conditions was done. Since the early 70's last century, Na burning and Na-based aerosol behaviour and their chemical composition had been the subject of experimental research projects and several computer codes had been developed to analyse these scenarios with relative success. However, all these codes had mostly focused on thermal-hydraulic consequences to evaluate the risk of containment overpressure and particle generation modelling had received much less attention.

According to the current international trend in the development of SFR severe accident codes consisted in taking advantage of the commonalities with LWR ones, i.e. adopt the main code architecture and programming and just include modifications for those phenomena which are SFR-specific. By modelling particle generation from Na pools and their subsequent in-containment evolution, this thesis means a significant contribution towards the understanding of the in-containment source term in SFRs.

Development of a Particle Generation model

A phenomenological Particle Generation (PG) model covering sodium-vapour burning and formation of sodium-oxide aerosols above an evaporating sodium pool has been developed with the objective to calculating the characteristics (number and size) of the particulate source term to the containment. Based on a flame sheet approach, the model articulates a suite of individual models: Na vaporization (diffusion layer approach), O₂ transport by air natural circulation (3D flow pattern modelling), Na-O₂ chemical reactions (instantaneous reactions and energy input) and vapour-to-particle conversion of Na-oxides (i.e., classical nucleation theory and heterogeneous condensation).

The particle formation process over a high temperature pool of Na ($T > 800$ K) requires the modelling of both thermal phenomena (i.e., Na vaporization from the pool surface and oxygen natural circulation from the atmosphere to the reaction zone) and physico-chemical phenomena (i.e., Na-oxygen chemical reactions and homogeneous and heterogeneous nucleation of sodium oxides vapours).

Based on a diffusion-layer approach, an expression for the flux of sodium vapour from the pool surface is given by taking into account the diffusive resistance of nitrogen to the sodium vapour movement toward the flame and assuming no sodium vapour concentration in the flame region.

Due to the foreseen boundary conditions over the pool at the time of oxidation, a steady 3D Computation Fluid Dynamics approach is employed based on the FLUENT code to determine the thermal-hydraulic boundary conditions in the region of interest, i.e., in the close vicinity of the sodium reaction zone. In this numerical simulation, the O_2 natural convection and the Na- O_2 chemical reactions as instantaneous are modelled. The resulting saturation-ratio map reveals the potential for nucleation at different locations over the pool: large saturation values in the close vicinity of the pool. In other words, most probably all evaporated Na would become particulate near to the pool surface. At this point, the major influence of the saturation pressures of oxide vapours underline the need for having sound data on this variable for these compounds.

The particle formation process includes homogeneous and heterogeneous nucleation. The homogeneous nucleation has been treated by an approach based on classical nucleation theory. This choice is supported by the higher complexity of other theories (involving additional uncertain parameters), the inherent uncertainty coming from the lack of information on sodium-oxides properties and the huge sensitivity of any homogeneous nucleation theory to variations in boundary conditions (i.e., temperature). As the prevailing conditions for heterogeneous nucleation fall into the kinetic regime, the growth mechanism of condensation on existing particles has been formulated using kinetic theory. Homogeneous nucleation and condensation are simultaneous and competitive processes. In our approximation, a single-burst approach has been adopted in which homogeneous nucleation can be neglected beyond the first burst of primary particles.

Validation of Particle Generation model

A partial validation of the PG model has been carried out based on the comparison with the sodium pool experiments of Newman and Payne (1978) in the range of validity of the PG model (pool temperature from 800 K on). The estimates-to-data agreement is outstanding. On the one hand, the experimental trend of increased burning rate with Na pool temperature is followed by the calculations. On the other hand, the data scattering helps predictions to be well within the measurements range. When comparing the PG results with SOFIRE code (a reputable sodium pool combustion model based on the surface combustion approach) predictions, the gas-phase reaction approach used in PG model is strengthened by the SOFIRE under-prediction of the thermal load to the containment and the airborne-particle loading relative to what could be expected in the case of an in-containment pool fire.

The PG model predictions have been analysed for a generic sodium-pool scenario. As expected, large saturation values are found throughout the spatial domain explored which result in very high particle concentrations just above the sodium pool. Thus, in lumped parameter codes, pools should be seen as aerosol generators where the generation rate depends on vaporization rate and nuclei size is to be estimated from nucleation rate theories.

Build-up of a zero-dimensional model

Particle generation from a Na pool fire is associated with substantial gradients of temperature, Na_xO_y vapours and oxygen concentrations as well as turbulent agitation in the region right over the thin reaction layer set up next to the pool surface. A detailed picture of the scenario looked mandatory to achieve a thorough understanding of the physic-chemical scenario set. Nevertheless, using 3D computational fluid-dynamics in the analysis seems presently unsuitable. In order to turn the PG model into a useful analytical tool in the current context of lumped-parameter codes in the SFR safety domain, a 0D version had to be built up.

Transposing the 3D PG model to 0D model has been achieved through adopting average Na-oxide vapour concentration and temperature within the domain in which particle generation takes place. For consistency purposes, the adaptation has been supported on three qualitative criteria: consistency with anticipated sensitivity to major environmental variables according to the 3D model; accuracy in the range of the 3D model uncertainty in the number of generated particles and the primary particle size; and compatibility with the lumped-parameter formulation in integral codes for BDBA analysis. In addition to these, the preservation of the total number of generated particles formed has been guaranteed. As a result, the 0D approximation gives a nucleation rate equation that keeps the major CNT dependencies and relies on average gas properties of the entire active volume.

Derivation of analytical correlations

Due to the unavailability of some key variables of the zero-model in lumped-parameter codes, analytical correlations relying on Na-pool dimension, temperature and O_2 -concentration have been derived.

Given the absence of experimental data on particle generation from sodium pool fires, an analytical database has been build up by running the 3D model under 132 cases covering all the foreseen scenarios. The 0D model performance has been tested against this

analytical database. By exploring the sensitivity of the model to variables governing dominant processes through the analytical database, the physical consistency of the 0D model has been confirmed and the key model trends stated. They are the pillars for the 0D correlations. The number of generated particles has been linearly correlated with the vaporization rate and potentially correlated with the pool diameter and the pool temperature. For the primary particle size, a correlation encapsulating the weak dependencies on pool diameter and temperature and the stronger decreasing effect of O₂ concentration observed has been provided. However, given the narrow interval of diameters found, it might be reasonable to consider 0.001 µm as the primary particle diameter of generated particles after sodium pool combustion.

Assessment of the extended ASTEC-Na code

In order to assess the extended ASTEC-Na CPA code with the implemented correlations, a methodology to identify the most suitable experiments among nearly 20 experiments related to Na fires found in the open literature has been developed. The methodology is based on the application, by order of priority, of 5 criteria: representativeness of boundary conditions, normal test execution (no test artefacts), multiple scales, number of key variables documented in the available literature and accuracy of available data. As a result, a total of three experiments were chosen from ABCOVE and FAUNA programs.

Two major observations have been done: the model does not adversely impact the code estimates with respect to more empirical alternative approaches; by using the model proposed, there is no need of user-defined ad-hoc parameters in the input deck concerning Na-based particles behaviour. Regarding code behaviour, the model predictions yield the same order of magnitude and trends as data, both in terms of suspended aerosol concentration and diameter and capture these variables evolution.

In conclusion, the new correlations are very suitable for use in a severe-accident code in terms of the negligible additional computational burden. The new correlations, by originating from simplifications of soundly-based physical modelling, remove the arbitrariness in the assumption of a fixed primary-particle size in the existing modelling. Limited comparisons with experiments imply that use of the new correlations increases confidence in prediction of the pool-fire particulate source term to the containment.

The PG model predictions show a promising response in terms of order of magnitude of airborne concentration, dominant depletion mechanism and particle size variation; however, it is worth underlining the need of further research along two axis:

more and better Na-specific models and further research to build a robust and extensive database that can be used both to support individual models development and to validate computational tools capable of capturing main footprints of severe accidents in containment so that Source Term estimates are considered reliable.

Investigation of safety and potential source terms will require development of additional Na-specific modelling. This is the case of partitioning – or hosting – of radio contaminants by different phases (liquid sodium, vapour/gas phase, oxide aerosols, hydroxide droplets, etc.). On the other hand, the update, adaptation and optimization of existing sodium spray-fire models is needed for currently developing integral safety tools for SFRs.

There is an outstanding need to build a robust and extensive database that can be used to support individual models development and to overcome certain difficulties found in the model development as the lack of information on fundamental Na-oxide vapours properties.

Furthermore, the open literature containing experimental data on postulated in-containment source term behaviour of SFRs is scarce. Besides, tests characterization are neither as thorough as desirable nor as accurate as necessary for validation purposes. The comparisons to data set are far from a thorough validation: the number of comparisons is too reduced due to scarcity of open data and often variables recorded are insufficient to qualify any of the models developed (most data come from integral tests and separate effect tests data are either lacking or difficult to scale up); in addition, measurements are often affected by large uncertainties that prevent even the general trend from being seen. Presently, the adapted code version with the PG model correlations is planned to be further tested against access-restricted experiments and a postulated reactor accident.

Chapter 7

PUBLISHED PAPERS

This section collects the publications in journals and conferences that have been performed from the work presented in this thesis.

7.1. International journals

L.E. Herranz, M. Garcia, M.P. Kissane, C. Spengler. A lumped parameter modelling of particle generation from Na-pool fires in SFR containments. *Progress in Nuclear Energy* 109 (2018) 223-232.

L.E. Herranz, M. Garcia, L. Lebel, F. Mascari, C. Spengler. In-containment source term predictability of Astec-Na: Major insights from data-predictions benchmarking. *Nuclear Engineering and Design* 320 (2017) 269-281.

M. Garcia, L.E. Herranz, M.P. Kissane. Theoretical assessment of particle generation from sodium pool fires. *Nuclear Engineering and Design* 310 (2016) 470-483.

L.E. Herranz, M. Garcia, S. Morandi. Benchmarking LWR codes capability to model radionuclide transport within SFR containments: an analysis of the Na ABCOVE tests. Nuclear Engineering and Design 265 (2013) 772-784.

L.E. Herranz, M.P. Kissane, M. García. Comparison of LWR and SFR in-containment source term: similarities and differences. Progress in Nuclear Energy 66 (2013) 52-60.

L.E. Herranz, M. García, M.P. Kissane. In-containment source term in accident conditions in sodium-cooled fast reactors: Data needs and model capabilities. Progress in Nuclear Energy 54 (2012) 138-149.

7.2. National Journals

L.E. Herranz, M. Garcia, L. Lebel, F. Mascari, C. Spengler. Benchmarking Astec-Na code capability to model source term within SFR containments. Nuclear España 380, 54-58 (2017). PREMIO MEJOR PONENCIA I+D+I 2016.

7.3. International conferences

L.E. Herranz, M. Garcia, M. Kissane. Particle generation during sodium pool fires in SFR beyond design basis accidents.: assessment of thermal hydraulic boundary conditions. Proceedings of ICAPP 2016. San Francisco, CA (USA), April 17-20, 2016. Paper 16706.

L.E. Herranz, M. Garcia, L. Lebel, F. Mascari, C. Spengler. Predictability of source term behavior in SFR containments. Proceedings of ICAPP 2016. San Francisco, CA (USA), April 17-20, 2016. Paper 16740.

M. García, L.E. Herranz, M. Kissane. In-containment nucleation in severe accidents in SFR: assessment of thermal hydraulic boundary conditions. Proceedings of ICAPP 2014. Charlotte (USA), April 6-9, 2014. Paper 14068.

Garcia M., Herranz L.E., Kissane M.P., 2013. Priority source term issues in SFRs: Towards enabling safety studies. Proceedings of ICENES 2013, Madrid (Spain), May 26-30, 2013.

Kissane M., Garcia-Martin M., Herranz-Puebla L.E., 2013. Major remaining uncertainties associated with source-term evaluation for SFR severe accidents. Proceedings of the International Conference on Fast Reactors and Related Fuel Cycles (IAEA).

M. García, L.E. Herranz. Modeling reactive aerosols in oxidizing atmospheres: severe accidents in sodium fast reactors. European Aerosol Conference (EAC). Granada (Spain), September 2-7, 2012.

L.E. Herranz, M. García, S. Morandi. LWR codes capability to address SFR BDBA scenarios: Modeling of the ABCOVE tests. Proceedings of ICAPP 2012. Chicago (USA), June 24-28, 2012. Paper 12048.

L.E. Herranz, M. García. Comparison of LWR and SFR in-containment source term: similarities and differences. Proceedings of ICAPP 2011. Nice (France), May 2-5, 2011. Paper 11434.

7.4. National conferences

L.E. Herranz, M. Garcia, L. Lebel, F. Mascari, C. Spengler. Benchmarking Astec-Na code capability to model source term within SFR containments. Reunión Anual de la SNE. Santander (España), 28-30 septiembre, 2016.

M. García, L.E. Herranz. Development of a zero-dimensional particle generation model in SFR-containments under accidental conditions. Reunión Anual de la SNE. A Coruña (España), 23-25 septiembre, 2015.

M. García, L.E. Herranz, M.P. Kissane. Modelling homogeneous nucleation in sodium fast reactors in BDBA conditions. Reunión Anual de la SNE. Valencia (España), 1-3 Octubre, 2014.

M.García, J. Penalva, M.P. Kissane, L.E. Herranz. Numerical simulation of liquid metal pool combustion. Reunión Anual de la SNE. Reus, Tarragona (España), 25-27 Septiembre, 2013.

M. García, L.E. Herranz. Assessing the LWR codes capability to address SFR BDBAs: Modeling of the ABCOVE tests. Reunión Anual de la SNE. Cáceres (España), 17-19 Octubre, 2012.

M. García, L.E. Herranz. Applicability of LWR aerosol models in the SFR domain: simulation of the ABCOVE experiments. Reunión Anual de la SNE. Burgos (España), 28-30 Septiembre, 2011.

L.E. Herranz, M. García. Major differences of in-containment source term behaviour between LWRs and LMFBRS. Reunión Anual de la SNE. Santiago de Compostela (España), 06-08 Octubre, 2010.

Chapter 8

NOMENCLATURE

a	area
A	empirical constant
A_{pool}	Na-pool surface
B	empirical constant
c_s	particle sticking coefficient
c_p	specific heat capacity
$\bar{c}$	mean molecular speed
C	particle concentration
C_i	particle mobility
C_{bl}	molar gas concentration between pool surface and flame
C_g	molar gas concentration above the flame
d_p	particle diameter

d_{pool}	Na-pool temperature
$d_{p_{\text{critm}}}$	correlated particle diameter
d_{0D}	particle diameter in the 0D PG model
$D_{i,m}$	diffusion coefficient for species i in the mixture
D_{Na}	diffusivity of sodium in the binary system N ₂ -Na
D_{O_2}	diffusivity of oxygen in the binary system N ₂ - O ₂
F	flow of molecules to the surface of one particle
G	Gibbs free energy
h_s	specific enthalpy
J_{CNT}	nucleation rate by Classical Nucleation Theory
J_{ICCT}	nucleation rate by Internally Consistent Classical Theory
J_i	diffusion flux of species i
k	turbulent kinetic energy
k_B	Boltzmann constant
Kn	Knudsen number
l_f	flame height
L	characteristic length
Le	Lewis number
m	mass
m_1	molecular mass
$\dot{m}_{\text{Na}}$	Na-vapour mass flow rate
$\dot{m}_{\text{Na}_{PG}}$	Na mass flow rate into particles
$\dot{m}_{\text{Na}_2\text{O}}$	generated aerosol mass of Na ₂ O

$\dot{m}_{Na_2O_2}$	generated aerosol mass of Na_2O_2
$\dot{m}_{O_2}$	oxygen mass flow rate
M_{Na}	Na molar weight
$M_{w,i}$	molecular weight of species, i
n	molecules concentration
Nu	Nusselt number
N_{AV}	Avogadro's number
N_{crtl}	correlated number of generated particles
N_{3D}	number of generated particles calculated with the 3D PG model
N_{0D}	number of generated particles calculated with the 0D PG model
N_1	number concentration of molecules
$\dot{N}_1$	average number concentration of molecules
p_{vap}	vapour pressure
p_{v_i}	cell vapour pressure
$\bar{p}_v$	average vapour pressure
p_{sat}	saturation vapour pressure
$p_{sat,Na}$	saturation vapour pressure of sodium
P	pressure
Pr	Prandtl number
q_j	heat flux component
r	particle radii
Ra	Rayleigh number
R_i	net rate of production by chemical reaction

S	saturation ratio
$\bar{S}$	average saturation ratio
Sc	Schmidt number
Sh	Sherwood number
S_i	rate of creation by addition from the dispersed phase plus any user-defined sources
S_{ct}	turbulent Schmidt number
t	time
t_c	characteristic time
T	temperature
$\bar{T}$	average temperature
T_f	flame temperature
T_i	cell temperature
T_{pool}	Na-pool temperature
u_i, u_j	Cartesian velocity components
$\mathbf{v}$	velocity vector
v_1	molecular volume
v_i	cell volume
v_i, v_j	particle volume
V	particle volume
V_{PG}	nucleation zone volume
x_i, x_j	Cartesian coordinates
X	O ₂ -Na stoichiometric ratio
X_{Na}	fraction of sodium on the pool surface

$X_{N2,f}$	fraction of oxygen in the flame
$X_{N2,p}$	fraction of oxygen on the pool surface
X_{O2}	fraction of oxygen
Y_i	local mass fraction of species, i
Y_P	mass fraction of any product species, P
Y_R	mass fraction of a particular reactant, R
z	collision rate per unit area (kinetic theory)

Greek symbols

β	agglomeration kernel
γ	agglomeration shape factor
ε_T	turbulent dissipation rate
λ	mean free path
μ	viscosity
μ_τ	turbulent viscosity
$\overline{\mu_i \mu_j}$	Reynolds stress tensors
$v'_{i,r}$	stoichiometric coefficient for reactant i in reaction r
$v''_{i,r}$	stoichiometric coefficient for product i in reaction r
ρ	density
ρ_{aero}	aerosol density
ρ_p	particle density
σ	surface tension
τ_{ij}	stress tensor component for i,j=1,2,3

ϕ_{Na}	molar flux of sodium vapour
ϕ_{O_2}	molar flux of oxygen
χ	dynamic shape factor
ω	specific turbulent dissipation rate

Chapter 9

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APPENDIXES

A. CLASSICAL NUCLEATION THEORY

Nucleation refers to the kinetic processes involved in the initiation of first order phase transitions in nonequilibrium systems. Two phase equilibrium states for a pure substance, e.g. vapour and liquid, occur at unique pairs of temperature T and pressure P . For two-phase vapour-liquid equilibrium, the pressure is referred to as the equilibrium vapour pressure (P_{ve}). If the actual pressure of the vapour (P_v) is larger than the equilibrium vapour pressure, the vapour is said to be supersaturated. The degree of supersaturation is defined by the saturation ratio:

$$S = \frac{P_v}{P_{ve}} \tag{A-1}$$

This new state of the vapour is either metastable or unstable. Metastable state refers to a state stable with respect to small fluctuations and unstable against perturbation in the form of a finite fluctuation. These two types of states are distinguished by their location with respect to the mean-field spinodal, which is illustrated in Fig. A-1. In this figure, a P - V phase diagram for a pure fluid with several isotherms based on a van der Waals Equation Of State (EOS) is shown. The heavy dome-shaped curve denotes the binodal line, the locus of two-phase, vapour-liquid equilibrium states, which ends at the critical point. The green solid line is a true isotherm whose intersections (e) with the binodal dome give the equilibrium pressure and volumes of the coexisting vapour-liquid phases. The true isotherms are flat in the two-phase region inside the dome. All mean-field EOSs are similar in that they artificially treat the fluid as a homogeneous phase with a continuously varying density inside the two-phase region. This unphysical oversimplification generates the “van der Waals loops” shown by the isotherms. The spinodal boundary separates mechanically stable regions (metastable states for which $(\partial P / \partial V)_T \leq 0$) from mechanically unstable regions (for which $(\partial P / \partial V)_T > 0$) as determined by the slope of the isotherms of the mean-field EOS. If the supersaturated vapour ($S \geq 1$) is in contact with its own liquid, it will condense until the vapour again reaches saturation.

Fig. A-1. Schematic P-V phase diagram for a pure substance.

If a container of volume V contains only pure vapour, at a suitably large supersaturation value ($S \geq 1$), droplets will start to form at an appreciable rate as a result of collisions among vapour molecules. This process of forming a droplet is known as homogeneous nucleation. If impurities are also present in the container, the supersaturated vapour will first condense on them in a process referred to as heterogeneous nucleation. Since nucleation plays a key role in many fields ranging from atmospheric application to material science, the study of nucleation has a long history and is currently receiving much attention stimulated by the development of new experimental and theoretical techniques to measure and predict nucleation rates.

The first comprehensive treatment of the thermodynamics of the nucleation process is due to Gibbs (Josiah Willard Gibbs, 1906). Gibbs showed that the reversible work required to form a nucleus of the new phase consists of two terms: a bulk (volumetric) term and a surface term. Later, in 1926 Volmer and Weber (Volmer and Weber, 1926) developed the first nucleation rate expression, by arguing that the nucleation rate should be proportional to the frequency of collisions between condensable vapour molecules and small droplets (critical clusters) of the new phase of a size, the critical size, that just allows spontaneous growth. A more detailed kinetic approach for the process of vapour-to-liquid nucleation was subsequently developed by Farkas (Farkas, 1927). The theory of Volmer, Weber and Farkas was extended a few years later by Becker and Döring (Becker and

Döring, 1935), Frenkel (Frenkel, 1939) and Zeldovich (Zeldovich, 1942) and is now known as Classical Nucleation Theory (CNT).

CNT is based on a set of rate equations for the change of the concentrations of clusters of different sizes as the result of the gain and loss of molecules (up to now monomers). Although phase change involves the evolution of heat, it is usually assumed that the temperatures of all clusters are equal to that of the background gas. This assumption implies that clusters undergo sufficient collisions with molecules of the background gas so that they become thermally equilibrated on a timescale that is short compared to that associated with the gain and loss of monomers (Seinfeld and Pandis, 2006).

To develop the rate equation for clusters it is assumed that clusters grow and shrink via the acquisition or loss of single molecules (Fig.A-2). Cluster-cluster collision events are so rare that they can be ignored. From the principle of microscopic reversibility, it follows that if cluster grow only by the addition of single molecules, evaporation also occurs one molecule at a time.

Fig. A-2. Cluster growth and evaporation processes.

In Fig. A-2, the number concentration of clusters containing i molecules (monomers) at a time t ($N_i(t)$) is governed by the following rate equation:

$$\frac{dN_i}{dt} = \beta_{i-1}N_{i-1}(t) - \gamma_i N_i(t) - \beta_i N_i(t) + \gamma_{i+1} N_{i+1}(t) \quad (\text{A-2})$$

where β_i is the forward rate constant for the collision of monomers with a cluster of size i (a so-called i -mer) and γ_i is the reverse rate constant for the evaporation of monomers from an i -mer.

Eqn. A-2 provides the basis for studying transient nucleation. Since the characteristic time needed to establish the steady-state cluster distribution is generally short compared to the timescale over which monomer concentrations might be changing, the distribution of clusters is assumed to be at a steady state corresponding to the instantaneous monomer concentration.

By defining $J_{i+1/2}$ as the net rate ($\text{cm}^{-3} \text{s}^{-1}$) at which clusters of size i become clusters of size $i+1$, the net rate is given by:

$$J_{i+1/2} = \beta_i N_i - \gamma_{i+1} N_{i+1} \quad (\text{A-3})$$

If, for a given monomer concentration (or saturation ratio S), the cluster concentrations can be assumed to be in a steady state, then the left-hand side (LHS) equals zero in Eqn. A-2. At steady state from Eqn. A-2, all the fluxes equal to a single and constant flux J :

$$J_{i+1/2} = J, \text{all } i \quad (\text{A-4})$$

From Eqn. A-2, the nucleation rate expression is derived by evaluating the forward and reverse rate constant (condensation/evaporation rate constants) by thermodynamic reasoning.

CNT is based on the definition of an hypothetical equilibrium distribution of clusters at supersaturated conditions $S > 1$. To do so, a constrain of a zero flux is imposed. This distribution obeys the Boltzmann distribution, i.e., the maximum probability distribution:

$$N_i^e = N_1 \exp(-\Delta G_i / kT) \quad (\text{A-5})$$

where N_1 is the total number of molecules in the system and ΔG_i is given by the Gibbs theory.

In the Gibbs theory, the free energy change due to the the transfer of i molecules from the vapour phase to form an i -mer of radius r is given by the following equation:

$$\Delta G_i = 4\pi\sigma r^2 - ikT \ln S \quad (\text{A-6})$$

Some assumptions are implicit in this expression: droplets as spherical, droplets of incompressible liquid and vapour phase as ideal gas.

This free energy change contains two terms. The first is the free-energy increase as a result of the formation of the i -mer surface area (mechanical process). This term always opposes droplet formation. The second term is the free energy decrease from the change in chemical potential due to the phase change from vapour to condensed phase. The negative sign before this term ensures that new phase formation ultimately lowers the free energy of the system. The surface tension σ is taken as that of the bulk liquid monomer, i.e., it is assumed that clusters of a small number of molecules exhibit the same surface tension as the bulk planar liquid. This assumption, called the capillarity approximation, is the major assumption underlying CNT.

The dependence of the Gibbs free energy on the cluster size (r) is illustrated in Fig. A-3. The ΔG increases monotonically when $S < 1$ and achieves a maximum at a certain critical i -mer radius (r^*) and then decreases. If the cluster size is lower than the critical radius, the surface term is dominant. As a result, the cluster has a higher tendency to shrink, i.e., to reduce its free energy, than to grow, i.e., to increase its free energy. On the other hand, if $r > r^*$, the volume term is dominant and the cluster has a higher tendency to grow than to shrink. The radius corresponding to the maximum, named critical radius, is calculated by setting $\partial\Delta G_i / \partial r = 0$:

$$r^* = \frac{2\sigma v_1}{kT \ln S} \quad (\text{A-7})$$

Furthermore, the corresponding value of number of molecules at the critical size is given by:

$$i^* = \frac{32\pi}{3} \frac{v_1^2 \sigma^3}{(kT)^3 (\ln S)^3} \quad (\text{A-8})$$

By substituting the critical radius in the Gibbs free energy, the free energy barrier height for nucleation is obtained:

$$\Delta G_i^* = \frac{4\pi}{3} \sigma r^{*2} = \frac{16\pi}{3} \frac{v_1^2 \sigma^3}{(kT \ln S)^2} \quad (\text{A-9})$$

This is the work of critical cluster formation and represents the barrier for the transition of the system into the new phase.

Fig. A-3. Gibbs free energy change for formation of a droplet of radius R_p from a vapour with saturation ratio S .

Turning to the expression for the equilibrium cluster distribution (Eqn. A-5) and substituting the Gibbs free energy change, it can be written:

$$N_i^e = N_1 \exp(-\theta i^{2/3} + i \ln S) \quad (\text{A-10})$$

where θ is the dimensionless surface tension:

$$\theta = (36\pi)^{1/3} v_1^{2/3} \sigma / kT \quad (\text{A-11})$$

Looking at Eqn. A-10, when $i=1$, the identity $N_i^e = N_1$ is not mismatch. The failure to approach this limit is a consequence of the capillarity approximation. However, it is not a fundamental problem as generally N_i^e is larger than 1 (Seinfeld and Pandis, 2006).

There have been several attempts to modify the formula for N_i^e and correct this problem. This is the case of the Internally Consistent Classical nucleation Theory (ICCT) by Girshick and Chiu (1990) through the definition of a steady-state cluster distribution at $S > 1$ with a constant net growth rate.

On the other hand, for sufficiently large i , Eqn. A-10 predicts unreal results: $N_i^e > N_1$ and therefore, this equation would be no longer valid when $iN_i^e \approx N_1$.

Even though these inaccuracies in $i \rightarrow 1$ and $i \rightarrow \infty$, this expression can be considered as accurate in the region where nucleation flux is desired, i.e., the region close to and below the critical size (i^*).

To determine the monomer escape frequency (forward rate constant) from an i -mer, the i -mer is assumed to be in equilibrium with the surrounding vapour. Then the i -mer vapour pressure equals the system vapour pressure and by the Kelvin equation it can be written:

$$p_i = p_1^e \exp\left(\frac{2\sigma v_1}{kTr}\right) \quad (\text{A-12})$$

At equilibrium the escape frequency (evaporation) equals the collision frequency (condensation):

$$\begin{aligned}\gamma_i = \beta_i &= \frac{p_1}{(2\pi m_1 kT)^{1/2}} \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 a_1 = \\ &= \frac{p_1^s}{(2\pi m_1 kT)^{1/2}} \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 a_1 \exp\left(\frac{2\sigma v_1}{kTr}\right)\end{aligned}\tag{A-13}$$

By combining this equation with the definition of i^* :

$$\gamma_i = \frac{p_1^s}{(2\pi m_1 kT)^{1/2}} \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 a_1 S^{\left\{(i^*/i)^{1/3} - 1\right\}}\tag{A-14}$$

Therefore, the nonequilibrium ratio can be expressed as:

$$\frac{\gamma_i}{\beta_i} = S^{\left\{(i^*/i)^{1/3} - 1\right\}}\tag{A-15}$$

At constrained equilibrium,

$$\beta_i N_i^e = \gamma_{i+1} N_{i+1}^e\tag{A-16}$$

and by operating with Eqn. A-14:

$$\frac{N_i^e}{N_1^e} = \frac{2^{5/2}}{\left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2} \prod_{j=2}^i S^{\left\{(i^*/j)^{1/3} - 1\right\}}\tag{A-17}$$

The constrained equilibrium cluster distribution is based on a supposed equilibrium existing for $S > 1$. The following boundary conditions are applied traditionally:

$$\begin{aligned}\lim_{i \rightarrow i_{\max}} N_i &= 0 \\ \lim_{i \rightarrow 1} \frac{N_i}{N_i^e} &= 1\end{aligned}\tag{A-18}$$

Then, from Eqns. A-3 and A-16 it can be written:

$$J = \beta_i N_i - \gamma_{i+1} N_{i+1} = \beta_i N_i^e \left[\frac{N_i}{N_i^e} - \frac{N_{i+1}}{N_{i+1}^e} \right] = \left(\sum_{j=1}^{i_{\max}-1} \frac{1}{\beta_j N_j^e} \right)^{-1} \approx \left(\int_0^\infty \frac{di}{\beta_i \cdot N_i^e} \right)^{-1}\tag{A-19}$$

By substituting the forward rate expression and the equilibrium distribution, the CNT expression for the nucleation rate is obtained (Seinfeld and Pandis, 2006):

$$J_{CNT} = \left(\frac{2\sigma}{\pi m_1} \right)^{1/2} \cdot v_1 \cdot N_1^2 \cdot \exp \left[-\frac{16\pi}{3} \cdot \frac{v_1^2 \sigma^3}{(k_B T)^3 (\ln S)^2} \right]\tag{A-20}$$

B. EXPERIMENTAL DATABASE ON NUCLEATION

As seen from the nucleation expression, all the inputs of the theory are experimental quantities which makes the theory easy and popular to use. For many years, it was impossible to measure nucleation rates accurately. Instead, what was usually determined experimentally was the critical supersaturation at which nucleation was observable at a significant rate, whose value was typically not known to better than one or two orders of magnitude. These critical supersaturation measurements were generally in good agreement with the predictions of CNT for many substances. Over the past twenty years, the development of new experimental techniques with improved precision has allowed the accurate measurement of nucleation rates for many substances. A compilation of the main homogeneous nucleation experiments found in the open literature is presented in the following table (Table B-1).

Table B-1. Experimental database on homogeneous nucleation.

Material	Technique	Ref.	Ranges (K)	Exptl.	Accuracy S
n-butanol	Two piston expansion chamber	Strey et al., 1986	232<T<292	J vs. S	-
n-propanol	Two piston expansion chamber	Strey et al., 1986	235<T<295	J vs. S	-
n-pentanol	Two piston expansion chamber	Strey et al., 1986	250<T<271	J vs. S	-
n-hexanol	Two piston expansion chamber	Strey et al., 1986	256<T<296	J vs. S	-
methanol	Two piston expansion chamber	Strey et al., 1986	230<T<274	J vs. S	-
ethanol	Two piston expansion chamber	Strey et al., 1986	239<T<295	J vs. S	-

Material	Technique	Ref.	Ranges (K)	Exptl.	Accuracy S
water	Expansion chamber (nucleation pulse method)	Viisanen et al., 1993	217<T<259	J vs. S	$\pm 3 \%$
n-butanol	Expansion chamber (nucleation pulse method)	Viisanen and Strey, 1994	225<T<265	J vs. S	$\pm 3 \%$
cesium	Thermal diffusion cloud chamber	Rudek et al., 1999	289<T<554	S_{onset} vs. T	13 % (298K) 9 % (554K)
sodium	Gas evaporation-condensation chamber	Martínez et al., 2005	555<T<646	S_{onset} vs. T	-

Fig. B-3. Homogeneous nucleation rates for n-butanol (Strey et al., 1986).

Fig. B-4. Homogeneous nucleation rates for n-propanol (Strey et al., 1986).

Fig. B-5. Homogeneous nucleation rates for n-pentanol (Strey et al., 1986).

Fig. B-6. Homogeneous nucleation rates for n-hexanol (Strey et al., 1986).

Fig. B-7. Homogeneous nucleation rates for methanol (Strey et al., 1986).

Fig. B-8. Homogeneous nucleation rates for ethanol (Strey et al., 1986).

Fig.B-9. Isothermal homogeneous nucleation rate J_{exp} as a function of supersaturation S for water (Viisanen et al., 1993).

Fig. B-10. Homogeneous nucleation rates for n-butanol (Viisanen and Strey, 1994).

Fig. B-11. Measured critical supersaturations for cesium versus maximum-rate plane temperature (Rudek et al., 1999).

Fig. B-12. Nucleation onset data for sodium versus temperature (Martínez et al., 2005).

C. NUCOND PROGRAM

The source code in FORTRAN 95 to calculate the vapour-to-particle conversion (homogeneous and heterogeneous nucleation) is presented in this appendix (NUCOND program). It collects boundary and initial conditions of the scenario given by FLUENT and generates the particle generation rate and primary particle size. In Fig. C-1 the flowchart is given.

Fig. C-1. Flow chart of NUCOND program (FORTRAN 95).

```

Program NUCONDcode
! * CNT - Na2Oy
! *****
! * 17nov2015
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! *
! * This program reads FLUENT ASCII file of data and returns
! * particle generation rate and primary particle size.
! *
! * Input file:
! * x-coord|y-coord|temp|press|node-numb|cell-vol|conc_mol-Na2Oy
! * *****
! *
implicit none

INTEGER :: i,tt,j
INTEGER :: ttend = 100 !nº timesteps
INTEGER :: st
DOUBLE PRECISION :: timestep

C ! Filenames variables de entrada
DOUBLE PRECISION :: xcoord, ycoord !input
DOUBLE PRECISION :: temp, press, nodenumb, cellvol, concmolNa2Oy !input
!K Pa m3 kmol/m3

C ! Filenames constants
DOUBLE PRECISION :: NA = 6.02252d23 !Avogadro number (molec/mol)
DOUBLE PRECISION :: kB = 1.3806488d-16 !Boltzmann constant (cm2.g/s2.K)
DOUBLE PRECISION :: R = 8.314 !J/K.mol (ideal gas law)
DOUBLE PRECISION :: MNa2O = 61.9789 ! PM(g/mol)
DOUBLE PRECISION :: mmNa2O = 1.02955d-22 !Mass 1molec of Na2O(g/molec)
DOUBLE PRECISION :: pi = 3.1415926536d-0

C ! Variables-TEMPERATURA
DOUBLE PRECISION :: psat !saturation vapour pres. (g/cm.s2) - ASTEC
DOUBLE PRECISION :: sigma !Na2O sup-tension(dyn/cm)- MoltenSaltsBook
DOUBLE PRECISION :: dens !Na2O density (g/cm3) - MoltenSaltsBook
DOUBLE PRECISION :: vm !molecular volume (cm3)
DOUBLE PRECISION :: kin !kinetic term_condensation (s/g.cm)

C ! Variables-TIEMPO (20)
DOUBLE PRECISION, dimension (100) :: Mcond ! (molec/m3)
DOUBLE PRECISION, dimension (100) :: pcond !vapour press. Na2O (g/cm.s2)
DOUBLE PRECISION, dimension (100) :: SR !saturation ratio
DOUBLE PRECISION, dimension (100) :: csize !critical size
DOUBLE PRECISION, dimension (100) :: cradius !(r*)
DOUBLE PRECISION, dimension (100) :: JCNT !Nucleation rate(part/cm3.s)
DOUBLE PRECISION, dimension (100) :: p !vapour press. Na2O (g/cm.s2)
DOUBLE PRECISION, dimension (100) :: M !(molec/m3)
DOUBLE PRECISION, dimension (100) :: Nnew !part.gen.condens(part/cm3)
DOUBLE PRECISION, dimension (100) :: dnew !tamaño partic.(cm)
DOUBLE PRECISION, dimension (100) :: B
DOUBLE PRECISION, dimension (100) :: C
DOUBLE PRECISION, dimension (100) :: d
DOUBLE PRECISION, dimension (100) :: dcond
DOUBLE PRECISION, dimension (100) :: N !(part/cm3)
DOUBLE PRECISION, dimension (100) :: Npart !(part)
DOUBLE PRECISION, dimension (100) :: N2D !(part)
DOUBLE PRECISION, dimension (100) :: N2Dcell !(part)

C ! Variables for operating
DOUBLE PRECISION :: kBT
DOUBLE PRECISION :: pre
DOUBLE PRECISION :: G
DOUBLE PRECISION :: e1

C ! OTRAS
DOUBLE PRECISION :: time !contador timestep (s)
CHARACTER :: SW
DOUBLE PRECISION :: dmin,dmax !rango bins
DOUBLE PRECISION, dimension (100) :: bin !nº bins
DOUBLE PRECISION, dimension (100) :: Nbin !partic en el bin(part/cm3)

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C      !Limpio variables
      Loop_CLEAN: DO tt=1,ttend
        d(tt)=0.0
        B(tt) = 0.0
        N(tt)=0.0
        C(tt)=0.0

        Mcond(tt) = 0.0
        pcond(tt) = 0.0
        SR(tt) = 0.0
        csize(tt) = 0.0
        cradius(tt) = 0.0
        JCNT(tt) = 0.0
        p(tt) = 0.0
        M(tt) = 0.0
        Nnew(tt) = 0.0
        dnew(tt) = 0.0
        dcond(tt)=0.0
        Npart(tt) = 0.0
        N2Dcell(tt) = 0.0
        N2D(tt) = 0.0
      END DO Loop_CLEAN

C      CLEAN
      dmin=0.0
      dmax=0.0

      Loop_CLEAN2: DO i=1,100
        bin(i)=0.0
        Nbin(i)=0.0
      END DO Loop_CLEAN2

C      *****
C      !Apertura archivos y lectura del input
      open (10,file='input.txt')
      open (30, file='distribucionFinal.txt')      !bin(i),Nbin(i)
      open (90, file='N2D.txt')

C      !doy valor a las variables de entrada
      read(10,*)nodenumb,xcoord,ycoord,cellvol,press,temp,concmolNaxOy

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C      *****
C      dmin = 1.0d-9
C      dmax = 2.0d-7
C
C      Loop_Bins: DO j=1, 100
C          bin(j)=dmin+j*((dmax-dmin)/100.0)
C      END DO Loop_Bins
C
C      *****
C      st=0
C      Loop_Celdas: DO WHILE (st==0)
C          *****
C
C          time=0.0
C          timestep = 1.0d-8
C
C          *****
C
C          *****
C      properties
C          e1 = 24.44009-(19399.60303/temp)-(2.26111*log(temp))
C          psat = 1.0d6*(10**e1)
C          sigma = 268.5-(0.0502*temp)
C          dens = 2.4797-(0.0004487*temp)
C          vm= mmNa2O/dens
C          kBT = kB*temp
C          kin = 1/(2*pi*mmNa2O*KB*temp)**(1.0/2.0)
C
C          *****
C          p(1) = 1.0d+4*concmolNa2Oy*R*temp
C          M(1) = p(1)/(kB*temp)
C          SR(1) = p(1)/psat
C
C          if (SR(1)<=1.0) then
C              JCNT(1) = 0.0
C              dnew(1) = 0.0
C              Nnew(1) = 0.0
C              print *, 'SR(1)<=1.0'
C
C          else
C              if (M(1)<1.0) then
C                  JCNT(1) = 0.0
C                  dnew(1) = 0.0
C                  Nnew(1) = 0.0
C                  print *, 'M(1)<1.0'

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else
  csize(1) = (32*pi/3)*((vm**2*sigma**3)/(kBT**3*log(SR(1))**3))
  cradius(1) = (2*sigma*vm)/(kBT*log(SR(1)))
  dnew(1) = cradius(1) * 2
  pre = (((2*sigma)/(pi*numNa20))**0.5)*(vm*(M(1)**2))
  G = -(csize(1)*log(SR(1))/2)
  JCNT(1) = pre*exp(G)
  Nnew(1) = JCNT(1)*1.0d-8
c | *****CRITERIO
  Npart(1)=Nnew(1)*cellvol*2*pi*1.0d+6

  IF (Npart(1)<1.0) THEN
    Npart(tt)=0.0
    dnew(1)=0.0
    Nnew(1)=0.0
    d(1)=dnew(1)
    N(1)=Nnew(1)
    Mcond(1) = M(1)
    pcond(1) = Mcond(1)*kBT
    B(1) = 0.0
    C(1) = 0.0
    dcond(1) = d(1)+B(1)
    d(1)=dcond(1)
c | *****FIN_CRITERIO
  ELSE
    d(1)=dnew(1)
    N(1)=Nnew(1)
    Mcond(1) = M(1)-Nnew(1)*csize(1)
    pcond(1) = Mcond(1)*kBT
    B(1) = 2*vm*kin*(pcond(1)-psat)*timestep
    C(1) = pi*kin*(pcond(1)-psat)*d(1)**2*N(1)*timestep
    dcond(1) = d(1)+B(1)
    d(1)=dcond(1)
    M(1)=Mcond(1)
  end if
END IF
end if |*****fin primer nucleo*****
c |
  N2Dcell(1) = Nnew(1)*cellvol*2*pi*1.0d+6
  N2D(1)= N2D(1)+N2Dcell(1)

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```

c | *****TIEMPO
| Loop_tiempo: DO tt=2,ttend
|
| time=time+timestep
| If (M(tt-1)>1) then
|
| M(tt) = M(tt-1)-C(tt-1)
| p(tt) = M(tt)*kBT
|
| B(tt) = 2*vm*kin*(p(tt)-psat)*timestep
|
| C(tt) = pi*kin*(p(tt)-psat)*d(tt-1)**2*N(1)*timestep
| dcond(tt) = d(tt-1)+B(tt)
| d(tt)=dcond(tt)
|
| else
| M(tt)=M(tt-1)
| p(tt)=M(tt)*kBT
|
| B(tt)=0
| C(tt)=0
| d(tt)=d(tt-1)
|
| end if
| END DO Loop_tiempo
c |
| SW="N"
| Loop_Locate: DO i=1,100
| IF (SW=="N") then
| IF (d(ttend)<bin(i)) THEN
| Nbin(i)=Nbin(i)+Nnew(1)*cellvol*2*pi*1.0d+6
| SW="Y"
| END IF
| END IF
| END DO Loop_Locate
| *****endcldp
|

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c      !limpio variables

      Loop_CLEAN3: DO tt=1,ttend
        d(tt)=0.0
        B(tt) = 0.0
        N(tt)=0.0
        C(tt)=0.0

        Mcond(tt) = 0.0
        pcond(tt) = 0.0
        SR(tt) = 0.0
        csize(tt) = 0.0
        cradius(tt) = 0.0
        JCNT(tt) = 0.0
        p(tt) = 0.0
        M(tt) = 0.0
        Nnew(tt) = 0.0
        dnew(tt) = 0.0
        dcond(tt)=0.0
      END DO Loop_CLEAN3

c
      read(10,*,IOSTAT=st)nodenumb,xcoord,ycoord,cellvol,press,temp,
& concmolNaxOy

      END DO Loop_Celdas

1090 write(90,1090) N2D(1)
      format(1(e11.5,2x)) !N2D.txt

      DO i=1,100
1030 write(30,1030) bin(i),Nbin(i) !distribucionFinal.txt
      format(2(e11.5,2x))
      END DO

      close(10) !cierra input.txt
      close(30) !cierra distribucionfinal.txt
      close (90) !N2D

      End Program NUCONDcode

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D.TESTS MATRIX

This section shows the theoretical case matrix set up for the 0D adaptation with a total of 160 cases. The case name indicates the O₂ content, the pool temperature and the pool diameter.

N°	Case name	O2 %	T_{pool} (K)	d_{pool} (m)
1	011100_0.1	5	1100	0.1
2	011000_0.1	5	1000	0.1
3	010950_0.1	5	950	0.1
4	010900_0.1	5	900	0.1
5	010850_0.1	5	850	0.1
6	011100_0.2	5	1100	0.2
7	011000_0.2	5	1000	0.2
8	010950_0.2	5	950	0.2
9	010900_0.2	5	900	0.2
10	010850_0.2	5	850	0.2
11	011100_0.5	5	1100	0.5
12	011000_0.5	5	1000	0.5
13	010950_0.5	5	950	0.5
14	010900_0.5	5	900	0.5
15	010850_0.5	5	850	0.5
16	011100_1	5	1100	1.0
17	011000_1	5	1000	1
18	010950_1	5	950	1
19	010900_1	5	900	1
20	010850_1	5	850	1
21	011100_2	5	1100	2
22	011000_2	5	1000	2
23	010950_2	5	950	2
24	010900_2	5	900	2
25	010850_2	5	850	2
26	011100_5	5	1100	5
27	011000_5	5	1000	5
28	010950_5	5	950	5
29	010900_5	5	900	5
30	010850_5	5	850	5
31	011100_7.5	5	1100	7.5
32	011000_7.5	5	1000	7.5
33	010950_7.5	5	950	7.5

N°	Case name	O2 %	T _{pool} (K)	d _{pool} (m)
34	010900_7.5	5	900	7.5
35	010850_7.5	5	850	7.5
36	011100_10	5	1100	10
37	011000_10	5	1000	10
38	010950_10	5	950	10
39	010900_10	5	900	10
40	010850_10	5	850	10
41	051100_0.1	5	1100	0.1
42	051000_0.1	5	1000	0.1
43	050950_0.1	5	950	0.1
44	050900_0.1	5	900	0.1
45	050850_0.1	5	850	0.1
46	051100_0.2	5	1100	0.2
47	051000_0.2	5	1000	0.2
48	050950_0.2	5	950	0.2
49	050900_0.2	5	900	0.2
50	050850_0.2	5	850	0.2
51	051100_0.5	5	1100	0.5
52	051000_0.5	5	1000	0.5
53	050950_0.5	5	950	0.5
54	050900_0.5	5	900	0.5
55	050850_0.5	5	850	0.5
56	051100_1	5	1100	1.0
57	051000_1	5	1000	1
58	050950_1	5	950	1
59	050900_1	5	900	1
60	050850_1	5	850	1
61	051100_2	5	1100	2
62	051000_2	5	1000	2
63	050950_2	5	950	2
64	050900_2	5	900	2
65	050850_2	5	850	2
66	051100_5	5	1100	5
67	051000_5	5	1000	5
68	050950_5	5	950	5
69	050900_5	5	900	5
70	050850_5	5	850	5
71	051100_7.5	5	1100	7.5
72	051000_7.5	5	1000	7.5
73	050950_7.5	5	950	7.5
74	050900_7.5	5	900	7.5
75	050850_7.5	5	850	7.5

N°	Case name	O2 %	T _{pool} (K)	d _{pool} (m)
76	051100_10	5	1100	10
77	051000_10	5	1000	10
78	050950_10	5	950	10
79	050900_10	5	900	10
80	050850_10	5	850	10
81	101100_0.1	10	1100	0.1
82	101000_0.1	10	1000	0.1
83	100950_0.1	10	950	0.1
84	100900_0.1	10	900	0.1
85	100850_0.1	10	850	0.1
86	101100_0.2	10	1100	0.2
87	101000_0.2	10	1000	0.2
88	100950_0.2	10	950	0.2
89	100900_0.2	10	900	0.2
90	100850_0.2	10	850	0.2
91	101100_0.5	10	1100	0.5
92	101000_0.5	10	1000	0.5
93	100950_0.5	10	950	0.5
94	100900_0.5	10	900	0.5
95	100850_0.5	10	850	0.5
96	101100_1	10	1100	1
97	101000_1	10	1000	1
98	100950_1	10	950	1
99	100900_1	10	900	1
100	100850_1	10	850	1
101	101100_2	10	1100	2
102	101000_2	10	1000	2
103	100950_2	10	950	2
104	100900_2	10	900	2
105	100850_2	10	850	2
106	101100_5	10	1100	5
107	101000_5	10	1000	5
108	100950_5	10	950	5
109	100900_5	10	900	5
110	100850_5	10	850	5
111	101100_7.5	10	1100	7.5
112	101000_7.5	10	1000	7.5
113	100950_7.5	10	950	7.5
114	100900_7.5	10	900	7.5
115	100850_7.5	10	850	7.5
116	101100_10	10	1100	10
117	101000_10	10	1000	10

N°	Case name	O2 %	T _{pool} (K)	d _{pool} (m)
118	100950_10	10	950	10
119	100900_10	10	900	10
120	100850_10	10	850	10
121	151100_0.1	15	1100	0.1
122	151000_0.1	15	1000	0.1
123	150950_0.1	15	950	0.1
124	150900_0.1	15	900	0.1
125	150850_0.1	15	850	0.1
126	151100_0.2	15	1100	0.2
127	151000_0.2	15	1000	0.2
128	150950_0.2	15	950	0.2
129	150900_0.2	15	900	0.2
130	150850_0.2	15	850	0.2
131	151100_0.5	15	1100	0.5
132	151000_0.5	15	1000	0.5
133	150950_0.5	15	950	0.5
134	150900_0.5	15	900	0.5
135	150850_0.5	15	850	0.5
136	151100_1	15	1100	1
137	151000_1	15	1000	1
138	150950_1	15	950	1
139	150900_1	15	900	1
140	150850_1	15	850	1
141	151100_2	15	1100	2
142	151000_2	15	1000	2
143	150950_2	15	950	2
144	150900_2	15	900	2
145	150850_2	15	850	2
146	151100_5	15	1100	5
147	151000_5	15	1000	5
148	150950_5	15	950	5
149	150900_5	15	900	5
150	150850_5	15	850	5
151	151100_7.5	15	1100	7.5
152	151000_7.5	15	1000	7.5
153	150950_7.5	15	950	7.5
154	150900_7.5	15	900	7.5
155	150850_7.5	15	850	7.5
156	151100_10	15	1100	10
157	151000_10	15	1000	10
158	150950_10	15	950	10
159	150900_10	15	900	10

N°	Case name	O2 %	T _{pool} (K)	d _{pool} (m)
160	150850_10	15	850	10
161	211100_0.1	21	1100	0.1
162	211000_0.1	21	1000	0.1
163	210950_0.1	21	950	0.1
164	210900_0.1	21	900	0.1
165	210850_0.1	21	850	0.1
166	211100_0.2	21	1100	0.2
167	211000_0.2	21	1000	0.2
168	210950_0.2	21	950	0.2
169	210900_0.2	21	900	0.2
170	210850_0.2	21	850	0.2
171	211100_0.5	21	1100	0.5
172	211000_0.5	21	1000	0.5
173	210950_0.5	21	950	0.5
174	210900_0.5	21	900	0.5
175	210850_0.5	21	850	0.5
176	211100_1	21	1100	1
177	211000_1	21	1000	1
178	210950_1	21	950	1
179	210900_1	21	900	1
180	210850_1	21	850	1
181	211100_2	21	1100	2
182	2101000_2	21	1000	2
183	210950_2	21	950	2
184	210900_2	21	900	2
185	210850_2	21	850	2
186	211100_5	21	1100	5
187	211000_5	21	1000	5
188	210950_5	21	950	5
189	210900_5	21	900	5
190	210850_5	21	850	5
191	211100_7.5	21	1100	7.5
192	211000_7.5	21	1000	7.5
193	210900_7.5	21	950	7.5
194	210900_7.5	21	900	7.5
195	210850_7.5	21	850	7.5
196	211100_10	21	1100	10
197	211000_10	21	1000	10
198	210950_10	21	950	10
199	210900_10	21	900	10
200	210850_10	21	850	10

E. INPUT FILES

This section contains an example of the input files for the NUCOND program. Each file consist of 7 columns for the cell coordinates (x and y), temperature and pressure, node number and molar concentration of sodium oxides (Na_xO_y) respectively. Each line corresponds to the boundary conditions in each cell of the analysed region. The input file corresponds to the test 211000_0.1 (case 137). In this test, the region of interest is formed by 21316 cells. Only the first 100 cells are included as an illustrative example.

nodenumber	x-coord	y-coord	cell-vol	press	temp	conc_mol
56173	0.00E+00	6.32E-02	7.7172E-09	101325	1351.15	1.8494E-03
56172	2.49E-03	6.32E-02	1.1579E-08	101325	1351.16	1.8493E-03
56175	0.00E+00	6.57E-02	7.6988E-09	101325	1362.43	1.8346E-03
56174	2.49E-03	6.57E-02	1.1551E-08	101325	1362.44	1.8345E-03
54753	4.98E-03	6.32E-02	2.8929E-08	101325	1351.17	1.8491E-03
56179	0.00E+00	6.07E-02	7.7125E-09	101325	1339.50	1.8645E-03
56178	2.49E-03	6.07E-02	1.1572E-08	101325	1339.50	1.8645E-03
54754	4.97E-03	6.57E-02	2.8918E-08	101325	1362.47	1.8343E-03
54758	4.97E-03	6.07E-02	2.8874E-08	101325	1339.48	1.8643E-03
54752	7.45E-03	6.31E-02	4.4896E-08	101325	1351.09	1.8489E-03
56169	0.00E+00	6.81E-02	7.6798E-09	101325	1373.24	1.8203E-03
56168	2.48E-03	6.82E-02	1.1519E-08	101325	1373.26	1.8202E-03
54755	7.46E-03	6.56E-02	4.5070E-08	101325	1362.41	1.8340E-03
54759	7.44E-03	6.06E-02	4.4712E-08	101325	1339.39	1.8641E-03
54749	4.96E-03	6.82E-02	2.8858E-08	101325	1373.29	1.8199E-03
56177	0.00E+00	5.82E-02	7.6869E-09	101325	1327.55	1.8800E-03
56176	2.48E-03	5.82E-02	1.1534E-08	101325	1327.54	1.8800E-03
52539	9.92E-03	6.31E-02	6.0242E-08	101325	1350.95	1.8486E-03
54757	4.97E-03	5.82E-02	2.8754E-08	101325	1327.49	1.8799E-03
52540	9.94E-03	6.56E-02	6.0502E-08	101325	1362.28	1.8337E-03
52544	9.90E-03	6.06E-02	5.9974E-08	101325	1339.22	1.8639E-03
54748	7.46E-03	6.81E-02	4.5135E-08	101325	1373.25	1.8196E-03
54756	7.42E-03	5.81E-02	4.4430E-08	101325	1327.36	1.8798E-03
56171	0.00E+00	7.06E-02	7.6987E-09	101325	1383.53	1.8064E-03
56170	2.49E-03	7.06E-02	1.1546E-08	101325	1383.54	1.8064E-03
52538	1.24E-02	6.30E-02	7.5101E-08	101325	1350.70	1.8483E-03
52545	1.23E-02	6.05E-02	7.4727E-08	101325	1338.96	1.8637E-03
52535	9.95E-03	6.81E-02	6.0708E-08	101325	1373.13	1.8192E-03
54750	4.98E-03	7.06E-02	2.8885E-08	101325	1383.56	1.8061E-03
52541	1.24E-02	6.56E-02	7.5433E-08	101325	1362.05	1.8333E-03
52543	9.88E-03	5.81E-02	5.9510E-08	101325	1327.17	1.8796E-03
56183	0.00E+00	5.57E-02	7.6573E-09	101325	1315.37	1.8958E-03
56182	2.48E-03	5.57E-02	1.1490E-08	101325	1315.36	1.8958E-03
54762	4.95E-03	5.57E-02	2.8610E-08	101325	1315.27	1.8957E-03
54751	7.47E-03	7.06E-02	4.5117E-08	101325	1383.54	1.8057E-03
50343	1.48E-02	6.30E-02	8.9959E-08	101325	1350.36	1.8481E-03

52542	1.23E-02	5.80E-02	7.4047E-08	101325	1326.88	1.8795E-03
54763	7.40E-03	5.56E-02	4.4091E-08	101325	1315.13	1.8956E-03
50348	1.48E-02	6.04E-02	8.9256E-08	101325	1338.60	1.8635E-03
52534	1.24E-02	6.81E-02	7.5720E-08	101325	1372.93	1.8188E-03
50344	1.48E-02	6.55E-02	9.0499E-08	101325	1361.74	1.8330E-03
52548	9.84E-03	5.56E-02	5.8960E-08	101325	1314.93	1.8955E-03
52536	9.96E-03	7.06E-02	6.0801E-08	101325	1383.47	1.8052E-03
56165	0.00E+00	7.31E-02	7.7334E-09	101325	1393.29	1.7930E-03
56164	2.50E-03	7.31E-02	1.1600E-08	101325	1393.29	1.7929E-03
50347	1.47E-02	5.79E-02	8.8144E-08	101325	1326.50	1.8793E-03
50342	1.72E-02	6.29E-02	1.0456E-07	101325	1349.93	1.8478E-03
54745	5.00E-03	7.31E-02	2.8974E-08	101325	1393.30	1.7926E-03
50349	1.71E-02	6.03E-02	1.0342E-07	101325	1338.15	1.8633E-03
52549	1.22E-02	5.55E-02	7.3257E-08	101325	1314.63	1.8954E-03
56181	0.00E+00	5.32E-02	7.6139E-09	101324	1303.02	1.9119E-03
56180	2.47E-03	5.32E-02	1.1425E-08	101325	1303.00	1.9119E-03
50339	1.49E-02	6.80E-02	9.0873E-08	101325	1372.62	1.8183E-03
54761	4.94E-03	5.32E-02	2.8401E-08	101324	1302.88	1.9119E-03
50345	1.72E-02	6.54E-02	1.0533E-07	101325	1361.32	1.8326E-03
52537	1.24E-02	7.06E-02	7.5969E-08	101325	1383.27	1.8047E-03
50346	1.71E-02	5.78E-02	1.0173E-07	101325	1326.03	1.8792E-03
54744	7.48E-03	7.31E-02	4.5024E-08	101325	1393.30	1.7922E-03
54760	7.37E-03	5.31E-02	4.3635E-08	101324	1302.71	1.9118E-03
50352	1.46E-02	5.54E-02	8.6968E-08	101325	1314.24	1.8954E-03
52547	9.80E-03	5.31E-02	5.8289E-08	101324	1302.50	1.9118E-03
49060	1.95E-02	6.02E-02	1.1615E-07	101325	1337.62	1.8631E-03
49055	1.96E-02	6.28E-02	1.1756E-07	101325	1349.41	1.8475E-03
50338	1.73E-02	6.79E-02	1.0593E-07	101325	1372.22	1.8179E-03
52531	9.96E-03	7.32E-02	6.0638E-08	101325	1393.25	1.7916E-03
52546	1.22E-02	5.30E-02	7.2371E-08	101324	1302.19	1.9117E-03
49059	1.94E-02	5.77E-02	1.1429E-07	101325	1325.47	1.8791E-03
50353	1.70E-02	5.53E-02	1.0007E-07	101324	1313.76	1.8953E-03
50340	1.49E-02	7.06E-02	9.1274E-08	101325	1382.97	1.8042E-03
49056	1.97E-02	6.53E-02	1.1881E-07	101325	1360.83	1.8322E-03
56167	0.00E+00	7.56E-02	7.7196E-09	101325	1402.50	1.7799E-03
56166	2.49E-03	7.56E-02	1.1580E-08	101325	1402.50	1.7799E-03
56187	0.00E+00	5.07E-02	7.5611E-09	101324	1290.58	1.9281E-03

56186	2.46E-03	5.07E-02	1.1345E-08	101324	1290.55	1.9281E-03
54766	4.92E-03	5.07E-02	2.8152E-08	101324	1290.40	1.9282E-03
50351	1.46E-02	5.29E-02	8.5810E-08	101324	1301.79	1.9117E-03
49061	2.18E-02	6.01E-02	1.2801E-07	101325	1337.02	1.8629E-03
54746	4.98E-03	7.56E-02	2.8927E-08	101325	1402.50	1.7796E-03
49054	2.19E-02	6.26E-02	1.2975E-07	101325	1348.84	1.8472E-03
52530	1.24E-02	7.31E-02	7.5953E-08	101325	1393.05	1.7910E-03
54767	7.34E-03	5.06E-02	4.3106E-08	101324	1290.23	1.9282E-03
49064	1.93E-02	5.52E-02	1.1244E-07	101325	1313.19	1.8953E-03
49058	2.17E-02	5.75E-02	1.2604E-07	101325	1324.85	1.8791E-03
49051	1.97E-02	6.78E-02	1.2000E-07	101325	1371.73	1.8174E-03
50341	1.73E-02	7.05E-02	1.0667E-07	101325	1382.59	1.8036E-03
54747	7.47E-03	7.56E-02	4.4910E-08	101325	1402.47	1.7792E-03
52552	9.75E-03	5.06E-02	5.7517E-08	101324	1290.01	1.9282E-03
50350	1.69E-02	5.28E-02	9.8553E-08	101324	1301.29	1.9117E-03
49057	2.20E-02	6.52E-02	1.3168E-07	101325	1360.29	1.8317E-03
52553	1.21E-02	5.05E-02	7.1364E-08	101324	1289.70	1.9281E-03
49065	2.16E-02	5.50E-02	1.2401E-07	101325	1312.54	1.8953E-03
47752	2.41E-02	5.99E-02	1.3985E-07	101325	1336.37	1.8627E-03
50335	1.49E-02	7.31E-02	9.1409E-08	101325	1392.74	1.7905E-03
52532	9.95E-03	7.56E-02	6.0475E-08	101325	1402.39	1.7786E-03
47747	2.43E-02	6.25E-02	1.4215E-07	101325	1348.21	1.8468E-03
49063	1.92E-02	5.26E-02	1.1061E-07	101324	1300.70	1.9118E-03
47751	2.40E-02	5.74E-02	1.3741E-07	101325	1324.16	1.8790E-03
50356	1.45E-02	5.04E-02	8.4556E-08	101324	1289.29	1.9282E-03
49050	2.21E-02	6.77E-02	1.3347E-07	101325	1371.20	1.8168E-03
56185	0.00E+00	4.82E-02	7.4676E-09	101324	1278.09	1.9446E-03

F. CPA* FEASIBILITY ANALYSIS

An analytical study to check the PG model feasibility has been developed prior its implementation in ASTEC-Na CPA. For that, an intermediate version of ASTEC-Na CPA has been build up. In this version (CPA_FS), the flame sheet approach has been introduced by implementing the sodium vaporization rate equation (Eqn. 47, see section 5.2 for more details). From here, the computation of sodium oxides fluxes is by assuming an infinitely fast or immediate particle generation.

AB1 test has been simulated with CPA_FS code to obtain the in-vessel THs conditions (pressure and temperature) and the sodium mass flux as outputs. These data are then used as input to analytically calculate the particle generation rate by the PG model correlation (Eqn. 45). The total aerosol mass is then obtained assuming spherical primary particles with a diameter given by Eqn. 46. For a direct comparison with experimental data (airborne concentration), the deposition effects calculated by CPA_FS are assumed and imposed in the predicted total aerosol mass with the PG model. In Fig. F-1, the experimental airborne concentration is compared with the analytically calculated suspended aerosol concentration by the PG model correlations. From the figure, predictions within experimental uncertainties indicate a suitable Na burning rate modelling by the implemented approach.

Fig. F-1. Airborne concentration.

G. SELECTION PROCESS OF THE VALIDATION TEST MATRIX

In order to assess the ASTEC-Na CPA code (CPA* up to now), a literature review of experimental information led to nearly 20 experiments related to Na fires, of which nearly half dealt with aerosol generation from pool fires. In table G.1, an overview of the available sodium pool fire experiments is given.

Table G.1. Sodium pool fire experiments overview.

	TVMA	AB1	AB2	AB7	F1-F2-F3	F5-F6
Geometry	Cubic	Cylindrical	Cylindrical	Cylindrical	Cylindrical	Cylindrical
Volume	400 m ³	852 m ³	852 m ³	852 m ³	220 m ³	220 m ³
Na mass delivered	110 kg	410 kg	472 kg	6.434 kg Na 354.6 g NaI	150-250-500 kg	350 kg
Na T	853.15 K	873.15 K	873.15 K	863.15 K	300-500-500 °C	480 °C
Pool fire burning area	1 m ²	4.4 m ²	4.4 m ²	0.93 m ²	2-2-12 m ²	2-4.9 m ²
Pool fire burn duration	5400 s	3600 s	3600 s	600 s	110-210-80 min	60-120 min
Atm. init. BC	21 % O ₂	20% O ₂ 300 K 0.125 MPa	21% O ₂ 293 K 0.128 MPa Steam addition	21% O ₂ 297 K 0.1184 MPa		21% O ₂ 298.15 K 1.03 kg/cm ²

The selection process for the most suitable experiments is based on a developed methodology based on the application of the following criteria by order of priority:

1. Representativeness of boundary conditions.
2. Normal test execution (no test artefacts).
3. Multiple scales.
4. Number of key variables documented in the available literature.
5. Accuracy of available data.

For the application of criteria 4, a table compiling the key variables documented by experiment has been build up (Table G.2).

Table G.2. Documented variables of sodium pool fire experiments.

	TVMA	AB1	AB2	AB7	F1-F2-F3	F5-F6
Facility geometry	<ul style="list-style-type: none"> – Geometry – Volume – Length – Width – Height 	<ul style="list-style-type: none"> – Geometry – Volume – Height – Diameter – Cylinder height – Horizontal section – Total horizontal surface – Shell surface – Total internal surface – Vessel steel mass – Leakage rate, % D at 10 psig 	<ul style="list-style-type: none"> – Geometry – Volume – Height – Diameter – Cylinder height – Horizontal section – Total horizontal surface – Shell surface – Total internal surface – Vessel steel mass – Leakage rate, % D at 10 psig 	<ul style="list-style-type: none"> – Geometry – Volume – Height – Diameter – Cylinder height – Horizontal section – Total horizontal surface – Shell surface – Total internal surface – Vessel steel mass – Leakage rate, % D at 10 psig 	<ul style="list-style-type: none"> – Geometry – Volume 	<ul style="list-style-type: none"> – Geometry – Volume – Height – Diameter – Wall area – Wall thickness
Init. BC	<ul style="list-style-type: none"> – O₂ concentration (%) 	<ul style="list-style-type: none"> – O₂ concentration (%) – Temperature – Pressure – Dew point 	<ul style="list-style-type: none"> – O₂ concentration (%) – Temperature – Pressure – Dew point 	<ul style="list-style-type: none"> – O₂ concentration (%) – Temperature – Pressure – Dew point 		<ul style="list-style-type: none"> – O₂ concentration (%) – Temperature – Pressure
Sodium Spill	<ul style="list-style-type: none"> – Na mass delivered – Na temperature – Pool fire burning area – Pool fire burn duration 	<ul style="list-style-type: none"> – Na mass delivered – Na temperature – Pool fire burning area – Pool fire burn duration – Na flow rate – Total aerosol release - as Na – Fraction of oxidized Na released 	<ul style="list-style-type: none"> – Na mass delivered – Na temperature – Pool fire burning area – Pool fire burn duration – Total aerosol release - as Na – Fraction of oxidized Na released Steam addition <ul style="list-style-type: none"> – Flow started, sec after time zero – Flow stopped, sec after time zero – Flow rate 	<ul style="list-style-type: none"> – Na mass delivered – Na temperature – Pool fire burning area – Pool fire burn duration – Na flow rate – Na flow duration – Na fall distance NaI aerosol source <ul style="list-style-type: none"> – NaI aerosol source – Start time – Stop time – Release rate – Total NaI released 	<ul style="list-style-type: none"> – Na mass delivered – Na temperature – Pool fire burning area – Pool fire burn duration – Na burning rate – Max. Na T – Reacted Na 	<ul style="list-style-type: none"> – Na mass delivered – Na temperature – Pool fire burning area – Pool fire burn duration
Data						
Atmosphere Composition	–	<ul style="list-style-type: none"> – Mole percent of O₂, N₂, Ar, CO₂, CO, H₂, He, CH₄ vs. time – Final O₂, % – Final dew point 	<ul style="list-style-type: none"> – Mole percent of O₂, N₂, Ar, CO₂, CO, H₂, He, CH₄ vs. time – Final O₂, % – Final dew point 	–	–	<ul style="list-style-type: none"> – O₂ concentration (%) vs. time

	TVMA	AB1	AB2	AB7	F1-F2-F3	F5-F6
THs	–	<ul style="list-style-type: none"> – Wall steel temperatures vs. time – Atm. T vs. time (at 8 locations) – Vessel P vs. time 	<ul style="list-style-type: none"> – Wall steel temperatures vs. time – Atm. T vs. time (at 8 locations) – Vessel P vs. time 	<ul style="list-style-type: none"> – Atm. T vs. time – P vs. time – Shell T vs. time 	<ul style="list-style-type: none"> – Atm. T vs. time (at 2 locations) (F1, F3) – Medium gas T 	<ul style="list-style-type: none"> – Atm. T vs. time – Sodium pool T vs. time
Chemical analysis		<ul style="list-style-type: none"> – Suspended aerosol (mass fraction) vs. time (Na₂O₂, Na₂CO₃, NaH, NaOH, H₂O) – Burn pan residue (%) (Total Na, metallic Na, Na₂O, NaOH, Na₂O₂, Na₂CO₃) – Reaction products 	<ul style="list-style-type: none"> – Burn pan residue (%) (Total Na, metallic Na, Na₂O, NaOH, Na₂O₂, Na₂CO₃) – Reaction products 	<ul style="list-style-type: none"> – Airborne mass (NaOH, NaI) vs. time 	<ul style="list-style-type: none"> – Reaction products Na₂O₂/Na₂O – % of Na as carbonate (r.H<3,=20,>50, %) (unknown test) 	
Aerosol behaviour	<ul style="list-style-type: none"> – Mean of mass concent.vs. time – Final mass distrib. (upward, vertical and downward facing surfaces) 	<ul style="list-style-type: none"> – Suspended mass concentration vs. time (Na and Total) – Settled mass (Na) (unshadowed and shadowed surfaces) – Plated mass – Distribution of deposited sodium within CV (horizontal, vertical and top head surfaces) 	<ul style="list-style-type: none"> – Suspended mass concentration vs. time (Na and Total) – Settled mass (g Na) (unshadowed and shadowed surfaces) – Distribution of deposited sodium within CV (horizontal, vertical and top head surfaces) 	<ul style="list-style-type: none"> – Final Mass Distribution (NaOH, NaI) 	<ul style="list-style-type: none"> – Max aerosol mass concent. – Suspended mass concentration vs. time (Na₂O₂) 	
Aerosol size	<ul style="list-style-type: none"> – AMMD vs. time – Sigma vs. time 	<ul style="list-style-type: none"> – AMMD vs. time – Sigma vs. time 	<ul style="list-style-type: none"> – AMMD vs. time – Sigma vs. time 	<ul style="list-style-type: none"> – AMMD (NaOH, NaI) vs. time – Sigma (NaOH, NaI) vs. time 	<ul style="list-style-type: none"> – Particle diameter vs. time (unknown test) 	

The criterion 4 is applied by the evaluation of the importance of key variables (3 to 1 from high relevance to low relevance) as follows:

Variables	Score
Source Term	
Suspended aerosol mass vs. time	3
Final mass distribution	2
AMMD vs. time	3
GSD	2
Thermal-Hydraulics	
Atmosphere temperature vs. time	2
Pressure vs. time	1
Wall temperature vs. time	2
Atmosphere composition vs. time	1

In table G.3 the quantification of the key variables by experiment is shown. In blue colour, the experiments with 8 points or more are highlighted.

Table G.3. Experiments rating.

Sodium pool fire	TVMA	AB1	AB2	AB7	F1	F2	F3	F5	F6
Quantif.	10	16	16	15	8	6	8	2	3

Fig. G.1. shows the selection of the experiments by applying the defined 6 criteria. As final result, the proposed experiments for CPA* validation are AB1, AB2 and F2.

Fig. G.1. Sketch of the screening out methodology.